

April, 1935

RUBBER CHEMISTRY AND TECHNOLOGY

Published under the Auspices of the
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VOLUME VIII

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RUBBER CHEMISTRY AND TECHNOLOGY

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RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the editor representing the Rubber Division of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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Rubber Division Activities

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New Committee on Crude Rubber

Two papers on crude rubber were presented before the Rubber Division in New York City on April 23, 1935. The first of these papers, by G. A. Sackett, presented the subject from the consumers' point of view, and showed what characteristics were desired. The second paper, by Edgar Rhodes of the Rubber Research Institute of Malaya, covered the subject from the producers' angle. He discussed in considerable detail the difficulties encountered in the Far East in producing a standard, uniform product.

Following a lengthy discussion from the floor, S. M. Cadwell, Chairman, summarized the subject with a statement that there was obviously a lack of understanding on the part of the producers as to what the consumers wanted and needed, and on the part of the consumers as to what the producers could furnish.

The Chairman then appointed a committee to be known as "The Crude Rubber Committee," whose function is to promote better understanding between producer and consumer.

The personnel of the Crude Rubber Committee is as follows: E. B. Babcock, Firestone Tire and Rubber Co.; W. A. Gibbons, U. S. Rubber Products, Inc.; G. A. Sackett, Goodyear Tire and Rubber Co.; J. C. Walton, Boston Woven Hose and Rubber Co.; Harold Gray, *Chairman*, B. F. Goodrich Company.

The function of this committee is to promote a better understanding between the producers and consumers of crude rubber, to act as a clearing house between the two groups for information on quality requirements of various crude rubbers, including latex, to exchange opinions on the value of new types of crude rubber, and to be of general service in other ways.

The committee intends to establish contact with the various technical agencies allied with the producers in order to solve the problems of quality requirements, methods of testing, and evaluation of new types of rubber, including latex, and to deal only with those problems which can be handled through these agencies.

The committee will concern itself only with the technical aspects of these problems, and in turn only with such aspects as can be made public.

New Books and Other Publications

The Science of Rubber. Edited by K. Memmler, Director of Staatliche Materialprüfungsamt at Berlin-Dahlem, Germany, in collaboration with L. Hock, E. Kindscher, A. Koch, H. Pohle, R. Pummerer, A. Schob, A. Zimmermann. Authorized English translation edited by R. F. Dunbrook and V. N. Morris of The Research Staff of the Firestone Tire and Rubber Co. Book Department, Reinhold Publishing Corp., 330 W. 42nd St., New York, 1934. Bibliography. Author Index. Subject Index. Illustrated with 213 figures in the text and 4 color plates. Cloth, 770 pages, $6 \times 9\frac{1}{2}$ inches. Price \$15.00.

In this volume rubber technology and manufacturing give way to the fundamentally scientific aspects of rubber. Following a brief historical introduction of the discovery and technical and economic development of rubber, the results of its scientific study on the part of many authorities are quoted and interpreted, with copious references to original sources. The scope of the work is outlined by the following table of contents: Introduction, Botany, Chemistry, Vulcanization, Chemical and Physical Testing Methods, Physics of Rubber, Physical Testing Methods, Microscopy of Technical Vulcanizates, Bibliography, Author Index, Subject Index.

The bibliography, covering 56 pages, includes 1746 entries, and is the most complete compilation of references to books and pamphlets on the cultivation, properties, and uses of rubber and allied substances ever published in one place. The editors and their associates deserve the unstinted praise of all interested in the solution of rubber scientific problems for this authoritative digest of research progress already achieved by rubber scientists the world over. [From the *India Rubber World*.]

Industrial Fabrics. A Handbook for Engineers, Purchasing Agents, and Salesmen. By George B. Haven. First Edition. Published by Wellington Sears Co., 65 Worth St., New York, N. Y. 1934. Flexible leather. Gilt edges. 538 pages, $5\frac{1}{4} \times 7\frac{3}{4}$ inches, 159 illustrations, 52 tables. Indexed. Price \$2.00.

This handbook of industrial fabrics represents a selection of material based on an experience acquired over a period of nearly a century. It is offered as a contribution to the progress of cotton textiles in serving the needs of American industry. Prof. George B. Haven, Editor-in-Chief, is in charge of textile research at the Massachusetts Institute of Technology and is author of the text-book "Mechanical Fabrics." His long experience in textile engineering and scientific approach to industrial problems identify him as a leading authority on the technology of textiles.

The book comprises 7 chapters as follows: Types of Cotton; Manufacturing Processes for the Cotton Fiber; Cotton Yarn; Uses of Industrial Fabrics; Organization and Properties of Industrial Fabrics; Laboratory Design and Practice; Specifications and Test Methods.

The arrangement and completeness of the information in text and tables will appeal to those interested in data on the industrial uses, specification, and testing of every variety of cotton fabric and yarns. To those engaged in the manufacture of rubber goods in which cotton is an important structural factor this book will prove an indispensable source of data on mechanical fabric specialties. [From the *India Rubber World*.]

Rubber. Its Antioxidants and Preservatives. A bibliography compiled by the Science Library and the Research Association of British Rubber Manufacturers, London, England. 1934. Science Library Bibliographical Series No. 151. Board covers, 8 × 13 inches, 82 pages, plus supplement and list of journals on rubber chemistry. Price 5s. 0d. net.

The scope of the work comprises the theory of antioxidants, storage of rubber, corrosion and deterioration, absorption of water, and other liquids, action of light, preservation in general, oil-, acid-, and liquid-resistant rubber, and antioxidants. The volume includes some 1500 references. It is classified by the universal decimal classification, the numbers used being controlled by preliminary classification of the entries at the Research Association of British Rubber Manufacturers.

The work forms part of a series of bibliographies, now numbering 151, on various branches of science and technology, which are prepared by the Science Library in response to individual demand or on the occasion of special exhibitions. A complete list of titles is given at the end of this number. If these carefully prepared and extensive bibliographies were better known, they would save much time of research workers in collecting information on special subjects.

To reduce the cost of preparation the publications are issued in mimeographed form. Copies of this or any number may be obtained direct from the Science Museum, South Kensington, London, S. W. 7. [From the *India Rubber World*.]

Mechanical Rubber Goods. Catalog No. 34. Distributed by the New York Belting and Packing Company, 1 Market Street, Passaic, N. J. 95 pp.

Providing a vast fund of practical information about hose, belting, packing, and miscellaneous mechanical rubber products, this catalog makes an interesting piece of literature for engineers, purchasing agents, and factory executives. Illustrations and complete information are given about each product manufactured by the company. Diagrammatic drawings give clear outlines of various applications. Tables giving belt speeds, steam pressure and temperatures, carrying capacities and dimensions, are included in the catalog. Numerous formulas on every-day problems are presented, with examples of their usage. [From *The Rubber Age* of N. Y.]

Goodrich Engineering Data of Industrial Rubber Goods. Published by the B. F. Goodrich Company, Akron, Ohio.

Containing 21 pages of useful information and describing more than 200 rubber items, this catalog of engineering data is designed to simplify the selection of belting, hose, and other mechanical rubber goods for industrial service. A section on transmission belting includes a discussion on the relative merits of rubber and leather, a review of belting requisites and helpful hints on installation. Supplementing the information on conveyor belting, hose, rubber lining, and many other products are glossaries, tables, and technical data. Printed attractively in two colors this booklet should be a valuable asset to purchasing agents of industrial concerns. [From *The Rubber Age* of N. Y.]

Statistical Bulletin of the International Rubber Regulation Committee. Brettenham House, 5-6 Lancaster Place, Strand, London, W. C. 2, England. Vol. 1, No. 1, January, 1935. This monthly publication, issued by the International Rubber Regulation Committee, is an attempt to give all the principal available statistics regarding rubber in compact form. The Committee has decided to make the Bulletin available to the public at a reasonable price. Copies are obtainable at one shilling each. Annual subscription (calendar year only) ten shillings. [From the *India Rubber World*.]

Rubber and Agriculture. The Rubber Growers' Association, 2, 3, and 4 Idol Lane, Eastcheap, London, E. C. 3, England. This booklet of 64 pages is fully illustrated and contains sections devoted to the use of rubber equipment for tractors, pneumatic tires for farm vehicles, rubber for cow stalls and in the dairy, rubber footwear and clothing, belting and hose, rubber in the farmhouse, and miscellaneous application in various items of equipment used in farming operations. [From the *India Rubber World*.]

Handbook of the Rubber Exhibition. Science Museum, South Kensington, London, England, November, 1934, April, 1935. This handbook, besides enumerating the exhibits, gives an historical survey of the rubber industry and an account of the story of rubber from the growth of the rubber tree to the many applications of the product. [From the *India Rubber World*.]

Proceedings of the Thirty-seventh Annual Meeting. Held at Atlantic City, N. J., June 25-29, 1934. Vol. 34. American Society for Testing Materials, 260 S. Broad Street, Philadelphia, Pa. Cloth. Illustrated. Subject and author indices. Part I, 1325 pages; Part II, 943 pages.

Part I is devoted to Committee Reports, New and Revised Tentative Standards, and Tentative Revision of Standards. New material of interest to rubber technologists will be found in the reports of Committee D-11 on Rubber Products, Committee D-13 on Textile Materials, and Committee D-9 on Electrical Insulating Materials. Two tentative methods of rubber testing are presented, D394-34T Test for Abrasive Resistance of Rubber Compounds, and D395-34T Test for Compression Set of Vulcanized Rubber.

Part II comprises the technical papers given at the thirty-seventh annual meeting of the society. Among these papers are three relating to rubber as follows: "The Testing of Rubber and Rubber-like Materials for Oil Resistance," O. M. Hayden, Discussion; "The Testing of Raw Materials for Rubber Compounding," B. S. Taylor; "Materials for Use in Structural Engineering Models, with Special Reference to Rubber Compounds," A. V. Karpov, Discussion. [From the *India Rubber World*.]

1934 Book of A.S.T.M. Tentative Standards. Published by the American Society for Testing Materials, 260 S. Broad Street, Philadelphia, Penna. 1250 pp. \$7.00.

The 1934 edition of the A.S.T.M. tentative standards, which are issued as proposed standards, contains 236 items, of which 48 are included for the first time. About 60 standards were revised in 1934 and appear in their latest approved form. These standards cover such fields as ferrous and non-ferrous metals, paints, varnishes, petroleum products, road materials, and rubber products. Among specifications which appear for the first time are those for insulated wire and cable (Class A, 30% *Hevea* rubber compound), vulcanized rubber (test for compression set), and rubber compounds (test for abrasion-resistance). In addition to the 236 tentative standards the 1934 edition includes all proposed revisions of standards which are published to elicit criticism before final adoption. Changes in 60 standards have been proposed. [From *The Rubber Age* of N. Y.]

Index to A.S.T.M. Standards and Tentative Standards. American Society for Testing Materials, 260 S. Broad Street, Philadelphia, Pa. This pamphlet is designed to be of service in determining whether the A.S.T.M. has issued any specifications or test methods on particular materials or subjects in the materials field. All the A.S.T.M. specifications and tests are listed in the current Index under appropriate

key words, and the items under a particular subject are arranged alphabetically according to the significant word in the title, thus facilitating use of the Index. A list in numeric sequence of the serial designations is also included. [From the *India Rubber World*.]

Produits Speciaux Pour L'Industrie Du Caoutchouc. Société Anonyme des Matières Colorantes & Produits Chimiques de Saint-Denis, 69 Rue de Miromesnil, Paris (8e), France. This publication is a loose-leaf binder collection of notes descriptive of special products for the rubber industry made by the Saint-Denis Color & Chemical Co., Paris, France. Preceding the description of the various accelerators are two technical articles. The first deals with time and temperature relations with respect to scorching; the second, with conditions of vulcanization corresponding to optimum mechanical properties, plateau effect, and the advantages of using two accelerators simultaneously. The main body of the work comprises a systematic description of the various accelerators, classified as to speed, and similar special data on antioxidants, rubber colors, etc. The volume contains a number of instructive graphs and will prove distinctly valuable to rubber compounders in their use of rubber chemicals. [From the *India Rubber World*.]

Tornesit. Issued by the Hercules Power Company, Wilmington, Delaware. 20 pp.

Paints, emulsions, binders, adhesives, and plastics can be formulated with Tornesit, a chlorinated rubber base, to contain strong chemical resistance. The chemical and physical properties of this base are outlined in this attractively printed booklet which is profusely illustrated. Details concerning its appearance, odor, inflammability, gravity, stability, moisture content, dilution data, and solubility are given. The preparation and application of Tornesit paints, including spraying and brushing methods, are discussed. Suggestions for the use of Tornesit are made. The booklet concludes with a brief history of chlorinated rubber and the chemistry of Tornesit. [From *The Rubber Age* of N. Y.]

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The Rubber Pendulum, the Joule Effect, and the Dynamic Stress-Strain Curve

W. B. Wiegand and J. W. Snyder

General Description.—The rubber pendulum is one of two devices (Wiegand, *Trans. Inst. Rubber Ind.*, 1, 141 (1925)) which, by employing the Joule effect, constitute rubber heat engines in that they continuously convert heat into mechanical work.

In Fig. 1 is shown the original pendulum.* It consists of an ordinary pendulum of slow period fitted with a rubber band, one end of which is attached to the bob; the other to the upright support. This rubber band is stretched to four or five times its original length. Behind the upright is a metal shield so arranged that when the bob has reached the extremity of its swing the rubber band is clear of the shield, during the rest of the oscillation being in its shadow. Behind the pendulum and shield is an electric heating element with a copper reflector. The pendulum is started by displacement from the center towards one or other extremity. As this is done the rubber band is increased in length. At the extremity of the oscillation the stretch band is exposed to the radiant heat from the element, the Joule effect is brought into play and the band tends to shrink, thus pulling back the bob. Directly the band moves back within the shadow of the shield it cools, relaxes, and so allows the bob to swing out to the other side. Thereupon the band is once more heated up, contracts and so repeats the oscillation, which continues as long as the heat energy is supplied. When the electric current is turned off the pendulum dies down.

The pendulum furnishes a convenient means of visualizing, and to some extent measuring, the thermodynamical implications of the Joule effect; the extent and consequences of "fatigue" in vulcanized rubber; the conditions for, and degree of, reversibility; and the way in which these properties vary with the state of strain, with the temperature, and with other conditions.

Operation.—In Fig. 2 is shown an improved design of the pendulum.†

The pendulum may be set up in two different ways, "bottom-heavy" and "top-heavy." The former, although practicable, involves a shorter period and approximately simple harmonic motion, a condition less favorable because of reduction in time available for cooling (within the shadow). The preferred arrangement is one in which the pendulum comes to rest at either extremity of swing. In practice this means that the center of gravity is above the fulcrum. The tension of the stretched

* Now in the Deutsches Museum, Munich. The assistance of H. F. Schippel, Design Engineer, B. F. Goodrich Co., Akron, Ohio, in the original construction of both heat engines is here gratefully acknowledged.

† Built by the Firestone Tire & Rubber Co., Akron, Ohio. The authors wish to acknowledge the courtesy of N. A. Shepard and his associates in connection with the incorporation of improved mechanical features. The weights are now threaded to the arm, thus making possible more accurate adjustment of the center of gravity. All knife edges and bearings are movable. Two yoke bearings are each fitted with combs, mounting at will from one to seventeen stationers' bands. This use of a plurality of small bands improves balance, rate of heat absorption and dissipation, and also prevents slippage and reduces friction.

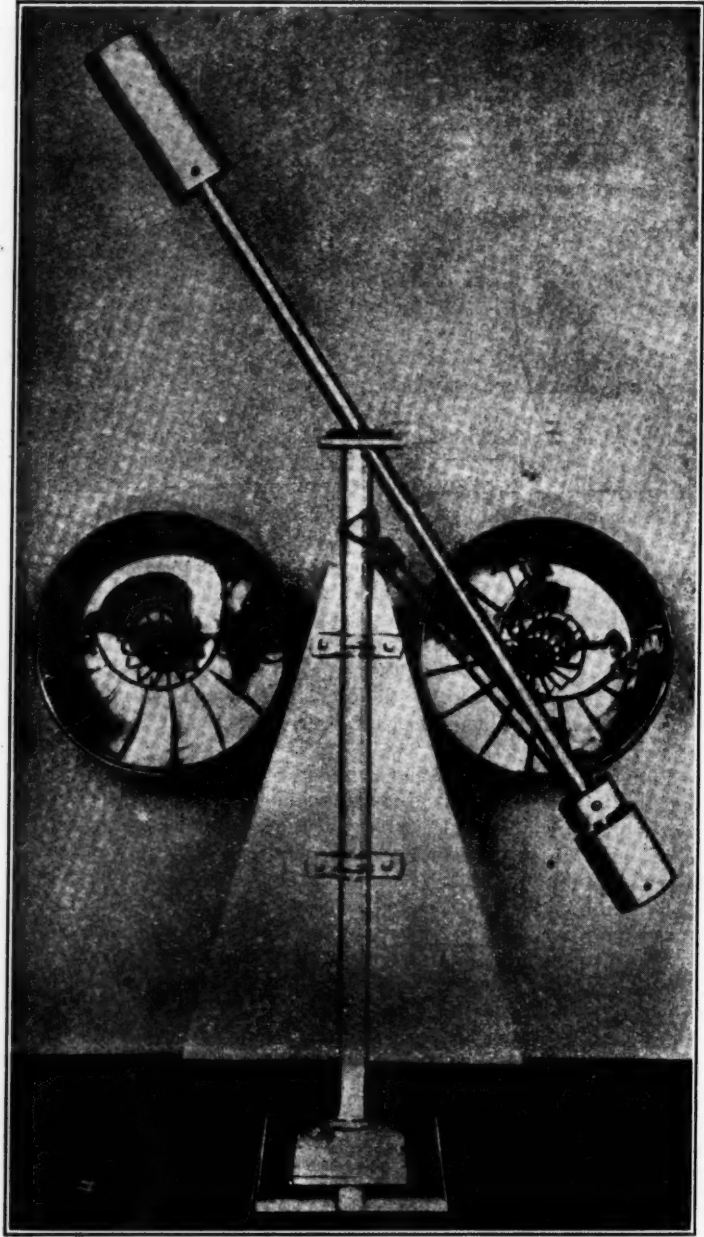


Figure 1

band or bands furnishes a restoring couple tending to make the pendulum less top-heavy.

Assembly.—The pendulum may be typically assembled in the following order (see Fig. 2).

K_3 is a knife edge upward, set on vertical support R , with bottom of piece 28 cm. above the base A . S is the shield symmetrically mounted on R with top of shield

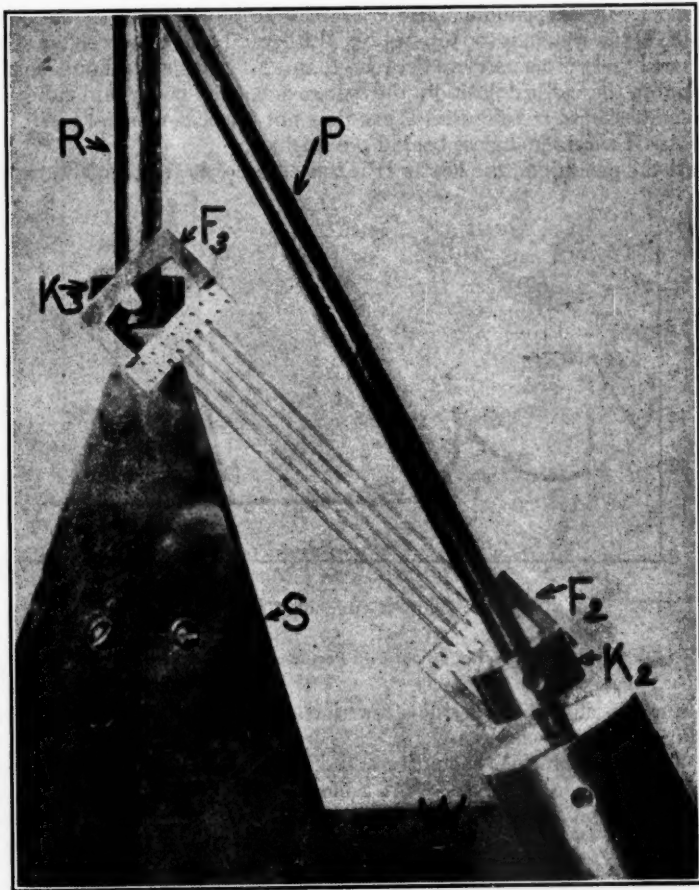


Figure 2

resting against bottom of K_3 . F_1 is the fulcrum or bearing set on R so that top edge of the piece is 11 cm. from the top of R ; on it rests K_1 , the knife edge downward placed on rod P so that the top edge of the piece is 25.8 cm. from the top end of P . (F_1 and K_1 are not shown on Fig. 2, being just above the top of the photograph.) K_2 is the knife edge downward, set with bottom edge of the piece 5.5 cm. from bottom end of P , and W_2 is the small weight threaded on lower end of P till top edge is 1.3 cm. from bottom edge of K_2 . W_1 (not shown in the figure) is the large weight threaded on the upper end of P till bottom edge of weight is 12.3 cm. above top

edge of K_1 . The system is now excessively top-heavy, P resting against one side of the bearing piece F_1 .

The two yokes, F_2 and F_3 , have two rows of pins over which rubber bands may be placed. There are seventeen sets of pins, but for the present set-up only the five center ones of the outside row are used. The rubber bands are of the stationers' type with a diameter of about 18 cm. if circular, or a length of 28 cm. if flattened.

Final adjustments are now necessary in accordance with the physical properties of the rubber. If the pendulum arm P comes to rest on one side so that it touches the side of F_1 , the system is too top-heavy. Either or both of the weights should be lowered until there is a small gap between P and F_1 . If the pendulum is at stable equilibrium in the vertical position, the system is bottom-heavy and either or both of the weights should be raised till P just does not touch F_1 when at rest. The radiant heater H is centered close behind the shield S.

To start the pendulum, the heater H is turned on. As the bands warm up, the

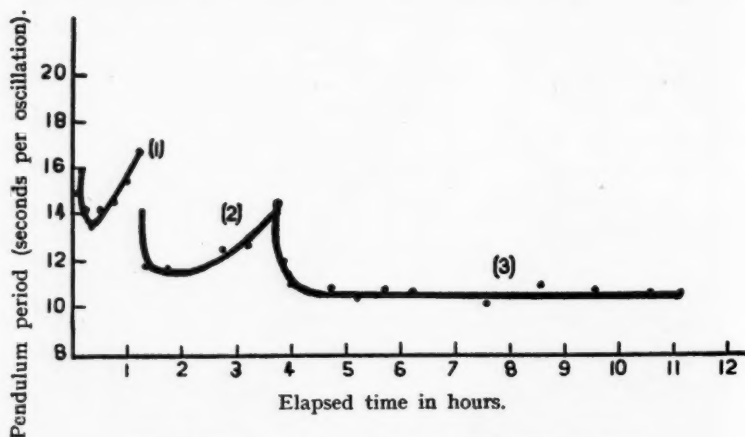


Figure 3—Effect of Fatigue on Period of Rubber Pendulum

pendulum will oscillate on one side a few times, finally cross over the center, and then begin complete oscillations.

The following precautions should be noted. The shield S should be set parallel to the short dimension of the base. All knife edges and bearings should be perpendicular to the plane of the shield. The set screw ends of both weights should be the first to go on P. If the pendulum swings more to one side than to the other, raise the base on the short side.

Fatigue or elastic after-effect requires attention in the adjustments, due, for example, to decay of tension in fresh bands. This decay naturally changes the restoring couple and so affects the center of gravity and period of oscillation. This effect requires elimination by allowing the assembled pendulum and bands to reach approximate equilibrium before proceeding to final adjustments. The influence of the constituent members of the pendulum assembly upon the operation, period, etc., furnishes a series of problems which are discussed below.

Factors Which Influence Performance

Fatigue and Secular Changes.—In Fig. 3 is shown the sequence of changes culminating in the attainment of constancy in the period of oscillation as a function of

elapsed time in hours. Two preliminary adjustments of the pendulum weights were sufficient to attain a constancy of period as in curve (3).

When the rubber bands are worked repeatedly over a given cycle the tensional stress decays, due to fatigue. This decline is rapid for the first few strokes, then gradually diminishes.

Fresh bands placed on the pendulum produce a restoring couple leaving the system still slightly top-heavy. As the bands warm up while the pendulum swings, the fatigue is more than counterbalanced by the increased force due to rising tem-

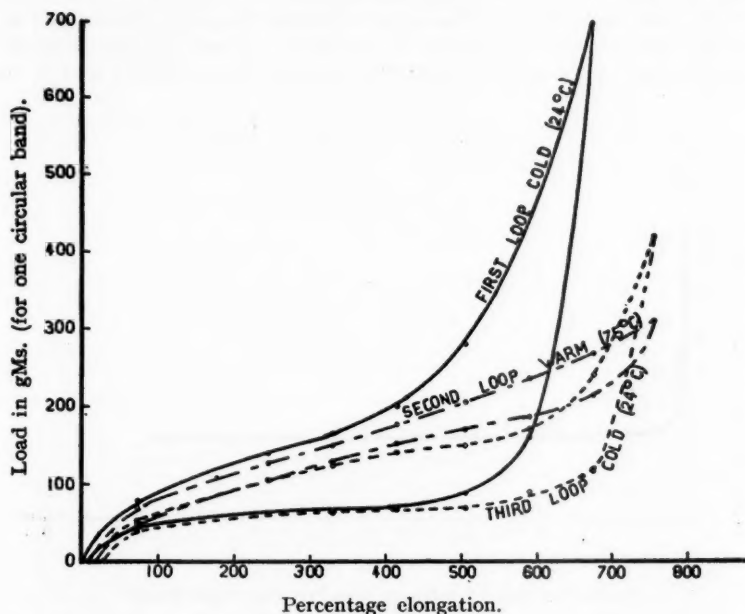


Figure 4—Hysteresis Loops of Cured Type S Bands at Room Temperature (24° C.) and at 75° C.

perature (Joule effect). This net increase in force shortens the period as shown in the initial drop of curve (1) of Fig. 3. From then on fatigue predominates, the pendulum becomes progressively more top-heavy, slows down, and finally stops. This is corrected by lowering top weight W_L . Once more the pendulum slows down and finally stops (curve 2). Again the weights are adjusted (curve 3). This time the cycle becomes reversible, fatigue has been worked out of the rubber, and the pendulum continues to oscillate at a uniform rate. After adjustments have been made in this way to compensate for fatigue, the pendulum has run for days with a minimum of attention.*

Since the time of oscillation is susceptible of exact measurement, using a stop watch over a number of swings, the pendulum may be used for the accurate determination of the elastic after-effect in vulcanized rubber, the attainment of reversibility being clearly marked by the period of oscillation reaching constancy.

Shield.—An increase in shield width causes at the same time a greater amplitude

* One model operated continuously for 150 days at the Chicago Exposition ("A Century of Progress Exposition") during the summer of 1933, with only occasional attention.

of swing and a slowing-up of the period. A decrease in shield width reduces the amplitude with a decrease in the period (see Table I).

TABLE I				
Shield width (times normal)	$1\frac{1}{2}$	$1\frac{1}{4}$	1	$\frac{1}{2}$
Period (seconds)	31	21	15	13

The pendulum may even be operated with no shield other than the supporting post itself. The amplitude in this case is very small and the period about eleven seconds.

Static Elongation or "Bore."—The distance between K_2 and K_3 determines in the vertical position the static elongation of the bands. Under the conditions of the experiments there was a critical elongation somewhat below 300 per cent at which

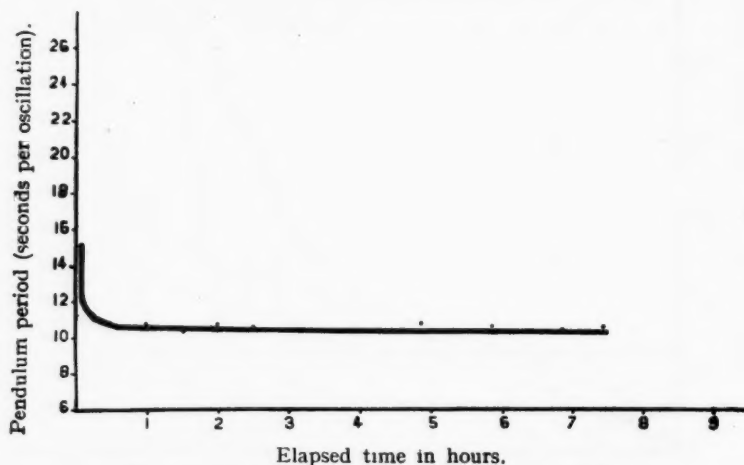


Figure 5—Rubber Pendulum with Five Pure Gum Bands

the pendulum ceased to operate. The upper limit of elongation could not be fixed due to limitations in design.

With the pendulum top-heavy and with 5 one-inch bands in place the relationships of Table II were obtained.

TABLE II		
Static elongation	300%	400%
Period (seconds)	10	13

This difference in elongation was brought about by raising or lowering K_3 . In so doing the stroke or difference in elongation between the vertical and side positions was altered and, as will be shown later, stroke has a profound effect on the pendulum operation.

The lower practicable limit of elongation is the point below which the Joule effect is absent, and no increase in tension is produced by an increase in temperature. Thereafter the Joule effect rises to a maximum as elongation is increased, then falls off to zero, and as the rubber approaches the breaking point becomes negative, thus fixing the upper limit of permissible elongation. As the elongation is increased the tension or restoring couple increases, thus making it necessary to readjust the weights to bring the system back to top-heaviness.

Cyclic Range of Elongation or Stroke.—Stroke may be increased by increasing the side displacement brought about by making the system more top-heavy; increasing the distance between K_3 and F_1 , and by decreasing the static elongation.

For short strokes of 0.6–1.0 cm. the pendulum is very sensitive and adjustments are delicate. Longer strokes facilitate regulation. Fresh bands will not operate

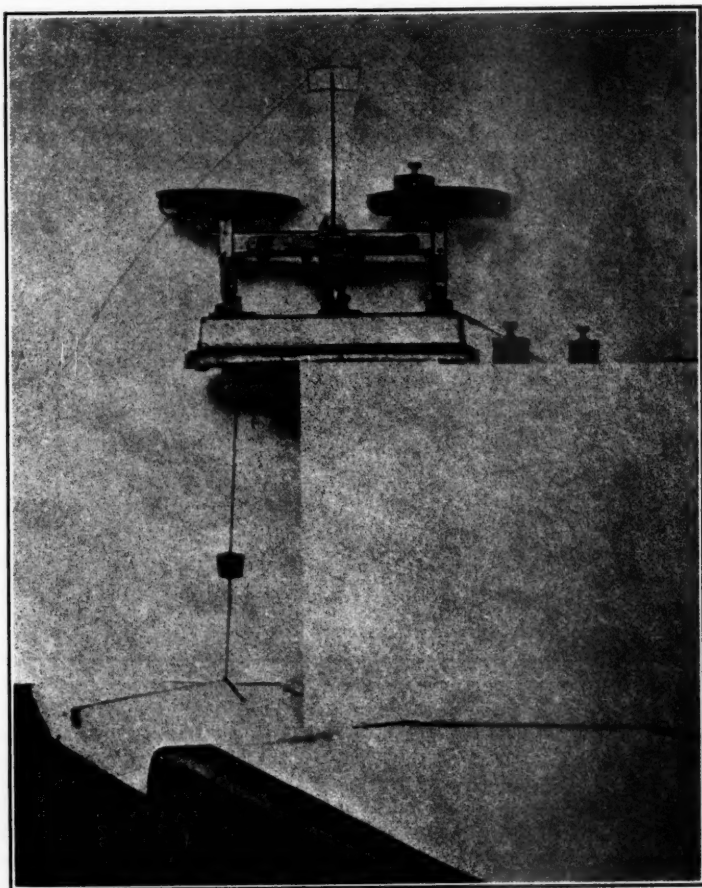


Figure 6

at short strokes. The bands must be thoroughly de-fatigued before use under these conditions.

Pre-Working.—The effect of working the bands was brought out above, the effect being to reduce the tension to an equilibrium value.

If the pendulum is operating regularly, a brief resting of the bands by momentarily reducing the static elongation will increase the tension of the bands to a point where the system becomes bottom-heavy and the pendulum will not run. On the other hand, a momentary increase of static elongation will decrease the band tension and the system will become so top-heavy as to prevent operation. When the

system is bottom-heavy, the pendulum will not run unless the bands have been pre-worked.

Surface of Bands.—The operation of the pendulum may be facilitated by blackening the surface of the bands. Heat absorption and dissipation are thus increased, the Joule effect is intensified, and the thermodynamic efficiency of the pendulum, viewed as a heat engine, is correspondingly improved.

Disposition of Members.—By adjustment of the two weights W_s and W_L and the knife edge K_1 , the system may be made bottom- or top-heavy. Raising either or both of the weights with K_1 fixed will increase top-heaviness. Lowering either or both will increase bottom-heaviness. With the weights fixed, raising K_1 will increase bottom-heaviness, while lowering K_1 will increase top-heaviness.

Although the pendulum oscillates most readily when the system is top-heavy, it

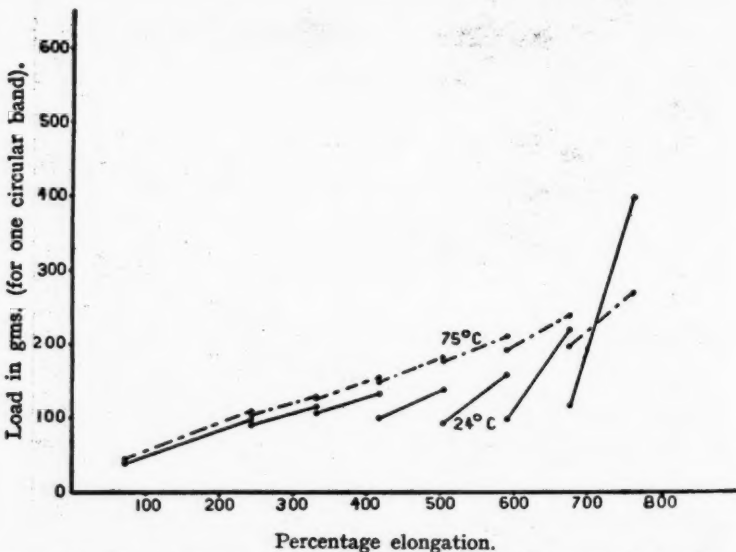


Figure 7—Dynamic Stress-Strain Curve for Reversible Cool and Warm Cycles (Carnot's Cycle Elements) for Type S Bands

can operate bottom-heavy. The conditions necessary are a system just barely bottom-heavy, a short stroke (about 0.6 cm.), and a static elongation of at least 300 per cent. The period of one cycle for such a set-up was 9 seconds, somewhat faster than for a top-heavy system. A slight raising of W_L made the system top-heavy and the period became 14 seconds.

When bottom-heavy, the pendulum must be started by hand. When top-heavy it is self starting. If the bottom-heavy pendulum is started by swinging it out to an amplitude greater than that for equilibrium, the amplitude will gradually decrease to the equilibrium value. If started at less than equilibrium amplitude it will slowly increase to the stable operating amplitude.

The bottom-heavy cycle approximates simple harmonic motion and has its maximum speed at the bottom of the swing. It is slowest at the extreme swing positions. The time for cooling is thus reduced by two factors, namely, the speed is greatest in the cooling zone, and the period of the bottom-heavy system is faster than that of the top-heavy. Contrasted to this, the top-heavy cycle is composed

of two simple harmonic-like motions. The maximum speed occurs about half-way between the vertical and the extreme positions. Thus the greatest velocity comes where least significant, namely, in the transition from heating to cooling, and *vice versa*. The time in the cooling and heating zones is relatively long. The times in these two zones while operating as a top-heavy cycle are shown in Table III.

TABLE III

Zone	Time (Seconds)
Heating	4.0
Cooling	2.3
Heating	4.0
Cooling	2.3
Total period	12.6

Thus two-thirds of the period was in this case in the heating zone and one-third in the region of cooling.

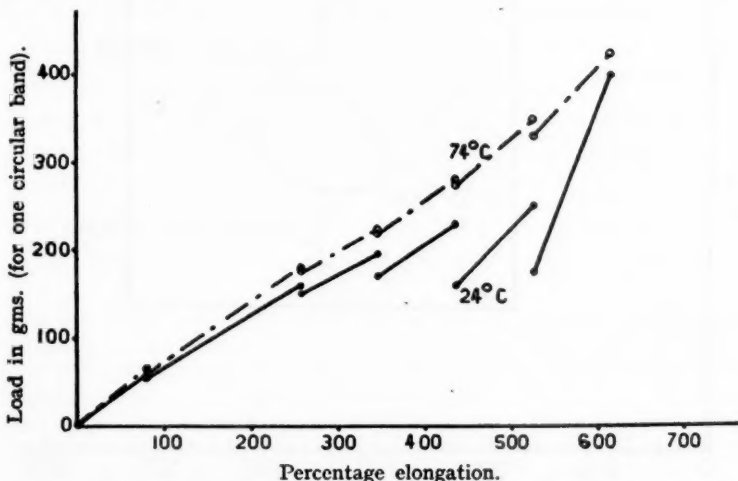


Figure 8—Dynamic Stress-Strain Curve for Reversible Cool and Warm Cycles (Carnot's Cycle Elements) for Type T Bands

The Rubber Pendulum and a Thermodynamical Study of the Rubber Stress-Strain Curve

The Effect of Successive Hysteresis Loops at Room Temperature and at 75° C.—A type "S" cured band (total sulfur, 2.15 per cent; combined sulfur, 0.95 per cent) was subjected to three successive hysteresis loops (see Fig. 4), first, at room temperature (24° C.); secondly, at 75° C., and, thirdly, at room temperature once more.

The position of these three loops illustrates how the previous history of a vulcanized rubber specimen is sufficient to influence profoundly the physical properties. It is seen from the above, for example, why the statement appears in the literature (Somerville and Cope, *India Rubber World*, 79, 64 (1928)) that higher temperatures cause a fall in the stress-strain curve and lowered modulus.

The same figure, however, also makes it clear why Bouasse and Carrière (*Ann. Faculté des Sciences de Toulouse*, 5, 257 (1903)) showed the opposite condition to obtain, namely, that the heated stress-strain curve stood higher on the paper and

gave higher modulus values than the loop at lower temperatures. The explanation seems to be that Bouasse tested the bands hot before he tested them cold, neither having reached equilibrium, and in the case of other workers the reverse condition probably obtained. This will serve briefly to illustrate the difficulty in arriving at valid conclusions as to the thermo-elastic properties of rubber in the entire absence of equilibrium or reversible conditions.

The Rubber Pendulum and Reversibility.—It has already been pointed out that after a preliminary period of fatigue elimination, the cured bands used in operating the rubber pendulum finally reached a condition where the restoring couple exerted on the pendulum reached constancy over relatively long periods of time. The criterion of this was the stability in the period of oscillation of the pendulum, and in

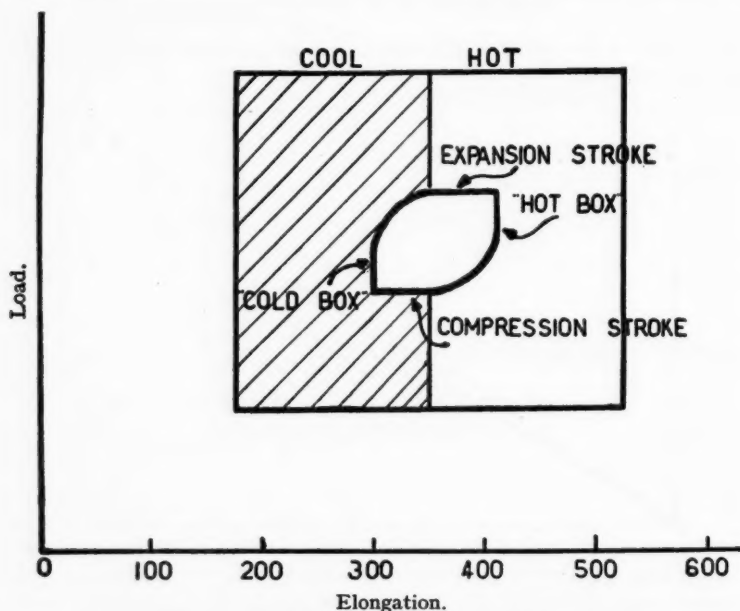


Figure 9—Carnot's Cycle for Rubber Pendulum (Diagrammatic)

Fig. 5 are shown actual results when the pendulum was equipped with five pure gum stationers' bands (type S). The attainment of this constancy in period suggested the possibility of generating a dynamic stress-strain curve from a series of successive cyclic elongations, each one being carried to the point of constancy or reversibility as in the pendulum.

A cyclic elongation of slightly less than 100 per cent was selected because it corresponded approximately to the stroke or range of elongation traversed by these bands when operating the pendulum. The set-up was as in Fig. 6. The results will be readily understood from two examples shown in Table IV.

It is seen that after five or six reversals a constant load is obtained. The rubber was then stretched for another increment of approximately 100 per cent elongation, allowed to retract, again stretched, and this miniature cycle repeated exactly as before. These successive cyclic elements were carried out for the whole stress-strain curve at room temperature and again at 75° C., and the results with type S

bands are shown in Fig. 7. The figure so obtained may be called a dynamic stress-strain curve at the respective temperature. It is seen that the 75° curve lies higher (up to a certain point) and that the slope of the constituent elements is entirely different for the two curves. In Fig. 8 are shown the dynamic stress-strain curves cool and warm, for the more highly cured stationers' type T band (total sulfur, 2.1 per cent, combined sulfur, 2.0 per cent). The slope of both cool and warm is higher, corresponding to increased cure, but the essential conditions are identical.

In both cases it will be noted that at about 300 per cent elongation a striking change occurs in the dynamic stress-strain curve at room temperature. The constituent elements begin at this point to separate from each other to an increasing extent, indicating the onset of a hysteresis condition. At the higher temperature, however, in both cases the dynamic stress-strain curve lies in a comparatively straight line obeying Hooke's law. The constituent elements of the curve continue substantially without displacement up to elongations close to the breaking point.

TABLE IV
DEVELOPMENT OF REVERSIBLE CYCLES FOR SINGLE BAND

At Room Temp. 24° C.		At 75° C.	
L330%	↔ L415%	L330%	↔ L415%
116 g.	↔ 137 g.	131 g.	↔ 157 g.
110	↔ 136	128	↔ 157
109	↔ 136	128	↔ 156
109	↔ 135	128	↔ 156
108	↔ 135	128	↔ 156

To the Joule effect, which causes an elevation in each of the constituent stress-strain elements, is added the effect of closing the gap. This latter effect must be regarded as entirely distinct from the Joule effect and, as will later be pointed out, can be simulated by means other than temperature.

Carnot's Cycle Elements.—The constituent elements of the dynamic stress-strain curve described above, when taken at room temperature and at a higher temperature, constitute the essential elements of Carnot's cycle as applied to the rubber pendulum (see Fig. 9). The essential steps in a gaseous heat engine are as follows: First, an expansion or power stroke at high temperature; secondly, a cooling off at constant volume; thirdly, a compression stroke at lower temperature; and, finally, a rise in temperature at constant volume.

The corresponding stages for rubber are as follows:

Expansion Stroke at High Temperature.—In the rubber pendulum this corresponds to the contraction of the rubber bands beginning at the outermost point of the swing of the pendulum and extending until they have passed within the shadow of the shield. During this time the bands are traversing what might be called an isotherm* strictly analogous to that of a gas, with the single exception that instead of a volume expansion the rubber undergoes a lateral expansion accompanied by a linear contraction, substantially without volume change. Looked at in this way, the power stroke of a rubber heat engine may legitimately be thought of as an expansion stroke.

* In Fig. 9 the expansion stroke is diagrammatically shown as horizontal because the radiant heat from the "hot box" more than compensates for the heat absorbed due to the slight contraction.

During the power stroke of the rubber heat engine, radiant energy from the heat source is being rapidly absorbed by the rubber and converted into work, but in this respect an important distinction must be kept in mind as between the rubber heat engine and the gas heat engine. In the latter case the heat taken up during the power or expansion stroke is all converted into mechanical work, because there is no change in the internal energy of a gas when its volume changes isothermally. In the case of rubber, the situation is quite different. During the power stroke of the rubber engine there is a marked increase in the internal energy. The exact amount of this energy change has not been experimentally determined, but has been estimated* to reach a value of over half the mechanical work done. Thus the heat absorbed by the rubber heat engine during its power stroke goes towards increasing the energy of state as well as towards useful mechanical work.

Cooling at Constant Volume.—The analogous stage in the rubber engine consists in the cooling off of the bands directly they pass into the shadow. At this point, when the angular displacement is small, the rate of change of elongation of the bands is also negligible. The rubber engine is practically at dead center. During this stage the bands radiate and conduct away heat, their tension relaxes, or, what is the same thing, they pass to a lower isotherm. This relaxation in the tension of the bands is no inconsiderable quantity. An experiment with the bands actually used in the rubber pendulum indicated that at an elongation of 400 per cent the bands supported a weight of 610 grams when placed within the shadow of the shield. When exposed to the radiant source they supported at the same elongation a load of 730 grams, an increase of 120 grams weight.

Compression Stroke at Lower Temperature.—In the case of the rubber engine this consists in the outward swing of the pendulum accompanied by stretching the rubber bands in one direction or compressing in the other two directions. The initial stage of this compression stroke occurs within the shadow, and so may be regarded as proceeding essentially along the lower isotherm or stress-strain curve. Directly the bands pass beyond the edge of the shield they begin to absorb radiant energy, heat up rapidly, their tension increases, or, in other words, the rubber begins to move upwards to higher stress-strain isotherms. As the rubber bands approach the end of their outward extension, their temperature rapidly rises, not only because of the radiant energy but because of the release of internal energy. At the end of the stroke the bands reach their highest temperature, the tension increases so that the final stage is reached.

Temperature Rise at Constant Volume.—When the rubber bands have reached the end of their swing they are receiving radiant energy from the source, but are suffering no change in length. The increase in pressure during this stage of Carnot's cycle as applied to a gas is exactly analogous to the increase in stress of the rubber bands as they pass upwards, by virtue of the Joule effect, through successive stress-strain isotherms. The Carnot's cycle for the rubber pendulum is now complete, and all is ready for the power stroke to begin again.

Carnot's Cycle Elements.—It will be noted that the elements for Carnot's cycle do not appear until about 300 per cent elongation and that they disappear at elongations between 600 and 700 per cent. There is therefore a region in the rubber stress-strain curve in which the Joule effect and the development of Carnot's cycles is possible, whereas for earlier and later stages in the stress-strain history of a specimen the conditions for the conversion of heat into work by means of a rubber heat engine do not obtain.

* Unpublished communication from R. H. Gerke, U. S. Rubber Company, General Laboratories. Calculations from the authors' data confirm Gerke's findings and indicate that the increase in internal energy may even exceed the work done at certain regions in the stress-strain curve.

This suggested that some definite change in the internal energy and therefore in the structure of vulcanized rubber takes place within the critical range of the curve, and that such changes might be explored by thermodynamical means.

Application of Second Law: Change in Internal Energy of Vulcanized Rubber with Elongation

Following the terminology of Gerke (*Ind. Eng. Chem.*, 22, 73 (1930)), let T = absolute temperature; f = force (tension) in grams; L = length (cms.); q = heat absorbed (calories); E = energy content (calories); W = work done by rubber = $-f dL$; C = heat capacity per gram = $\frac{dq}{dT}$; S = entropy ($ds = \frac{dq}{T}$).

For reversible cyclic elements we have the following (see Gerke, *loc. cit.*):

From the First Law

$$dq = dE + dW \quad (1)$$

From Second Law

$$Tds = dE + dW = dE - fdL \quad (2)$$

$$\text{Whence for constant } T, f = -T \left(\frac{\partial S}{\partial L} \right)_T + \left(\frac{\partial E}{\partial L} \right)_T \quad (3)$$

$$\text{Differentiating, } \left(\frac{\partial f}{\partial T} \right)_L = -T \left(\frac{\partial^2 S}{\partial T \partial L} \right) - \left(\frac{\partial S}{\partial L} \right)_T + \left(\frac{\partial^2 E}{\partial T \partial L} \right) \quad (4)$$

Similarly for constant L

$$(\partial S)_L = \left(\frac{\partial E}{\partial T} \right)_L \quad (5)$$

and,

$$\left(\frac{\partial S}{\partial T} \right)_L = \frac{1}{T} \left(\frac{\partial E}{\partial T} \right)_L \quad (6)$$

$$\text{differentiating, } \left(\frac{\partial^2 S}{\partial T \partial L} \right) = \frac{1}{T} \left(\frac{\partial^2 E}{\partial T \partial L} \right) \quad (7)$$

Combining (7) and (4),

$$\left(\frac{\partial f}{\partial T} \right)_L = - \left(\frac{\partial S}{\partial L} \right)_T \quad (8)$$

Combining (8) and (3),

$$\left(\frac{\partial E}{\partial L} \right)_T = f - T \left(\frac{\partial f}{\partial T} \right)_L \quad (9)$$

Thus a relationship is established between the change in the internal energy of the rubber and the change in tension per unit change of temperature. This makes possible the experimental determination of energy transformations without actual measurement of heat transfers.

For non-reversible elements the following arrangement of equation (9) is useful.

$$f' = \left(\frac{\partial E}{\partial L} \right)_T + T \left(\frac{\partial f}{\partial T} \right)_L + R \quad (10)$$

where f' is the non-reversible force and R is the frictional resistance of extension.

Let f'' = non-reversible force of retraction.

$$\text{Then } f'' = \left(\frac{\delta E}{\delta L}\right)_T + T \left(\frac{\delta f}{\delta T}\right)_L - R.$$

$$f' - f'' = 2R \text{ or } R = \frac{f' - f''}{2} \quad (11)$$

Experimental Determination of $\left(\frac{\delta E}{\delta L}\right)_T$.—From equation (9) may be determined the change in internal energy with increasing elongation in terms of the tensional stress, f , the absolute temperature, and $\left(\frac{\delta f}{\delta T}\right)_L$. The latter expression represents the Joule effect proper, namely, the change in the force or load per unit change in temperature at constant length.

For the dynamic element between given elongations the mean value for $\left(\frac{\delta E}{\delta L}\right)_T$ was obtained by taking the arithmetic mean of the values calculated for the extremes of the element. A typical example of such a calculation follows.

TABLE V
EFFECT OF TEMPERATURE ON LOAD AT CONSTANT LENGTH
TYPE T BAND

Elongation	Load	
	24° C.	74° C.
346%	172 gm.	220 gm.
435%	231 gm.	282 gm.

$$\left(\frac{\delta E}{\delta L}\right)_T = f - T \left(\frac{\delta f}{\delta T}\right)_L \quad (9)$$

at 346 per cent elongation

$$\left(\frac{\delta E}{\delta L}\right)_T = 172 - 297 \left(\frac{220 - 172}{74 - 24}\right) = -113 \text{ grams}$$

at 435 per cent elongation

$$\left(\frac{\delta E}{\delta L}\right)_T = 231 - 297 \left(\frac{282 - 231}{74 - 24}\right) = -72 \text{ grams.}$$

Mean value for above element

$$\left(\frac{\delta E}{\delta L}\right)_T = -92.5 \text{ grams.}$$

The results for the type *S* bands are shown in Fig. 10 and for the more highly cured type *T* bands in Fig. 11.

In both cases an interesting result appears, namely, that for small elongations up to about 350 per cent there is an increase in internal energy per unit change in length. After this point, however $\left(\frac{\delta E}{\delta L}\right)_T$ crosses the zero point and rapidly assumes increasingly negative values. This condition persists for elongations up to about 700 per cent. Between 500 and 600 per cent, the internal energy curve once more turns upward, crosses the zero line and again becomes positive. (In the case of the more highly cured band, rupture of the specimen occurred before these final segments of the curves could be obtained.)

The course of the values for $\left(\frac{\delta f}{\delta T}\right)_L$, that is, the increase in force per unit increase in temperature, assumes a complementary value, remaining small for elongations below 350 per cent, and then increasing rapidly to a maximum at between 500 and 600 per cent and thereafter declining.

These values for change in force and change in internal energy clearly portray the striking change in internal structure which goes on in what might be called the Joule effect or "heat engine" region of the vulcanized rubber stress-strain curve.

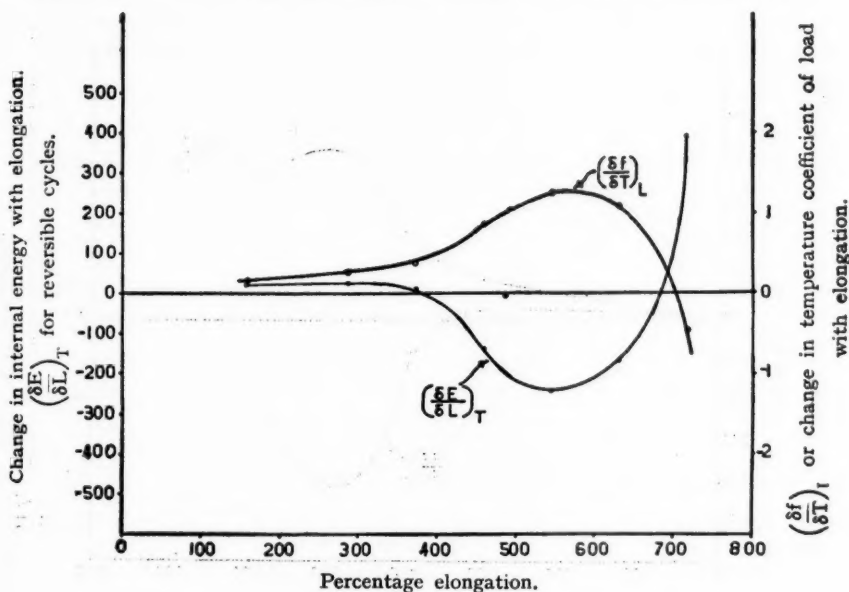


Figure 10— $\left(\frac{\delta f}{\delta T}\right)_L$ and $\left(\frac{\delta E}{\delta L}\right)_T$ for Type S Bands

Experimental Data from Other Sources.—Some unpublished experiments on the Joule effect by Schippel* have been subjected to similar analysis. Schippel's work was done at relatively low elongations where the internal energy increased with increasing elongation. Typical values are shown in Table VI.

TABLE VI
FROM SCHIPPEL'S DATA

Elongation	$\left(\frac{\delta E}{\delta L}\right)_T$
190%	+88 g.
264%	+97 g.

Schippel's experiments were carried out under entirely different conditions, but confirm the authors' findings as to the positive values for $\left(\frac{\delta E}{\delta L}\right)_T$ at elongations below 300 per cent.

* The authors are indebted to H. F. Schippel, Chief Design Engineer of the B. F. Goodrich Co., Akron, Ohio, for communicating the results of some unpublished experiments.

Gerke obtained the following values.* $\left(\frac{\delta E}{\delta L}\right)_T = -118$ grams at 620 per cent elongation. Although only a single determination, this value confirms the change of $\left(\frac{\delta E}{\delta L}\right)_T$ to strongly negative values at higher elongations.

Thus, the data of Schippel and Gerke fit into the general picture shown above. They represent various points along the internal energy curve which must now be recognized as highly variable and which indicates that Joule effect phenomena are concentrated within a rather sharply defined region of the curve.

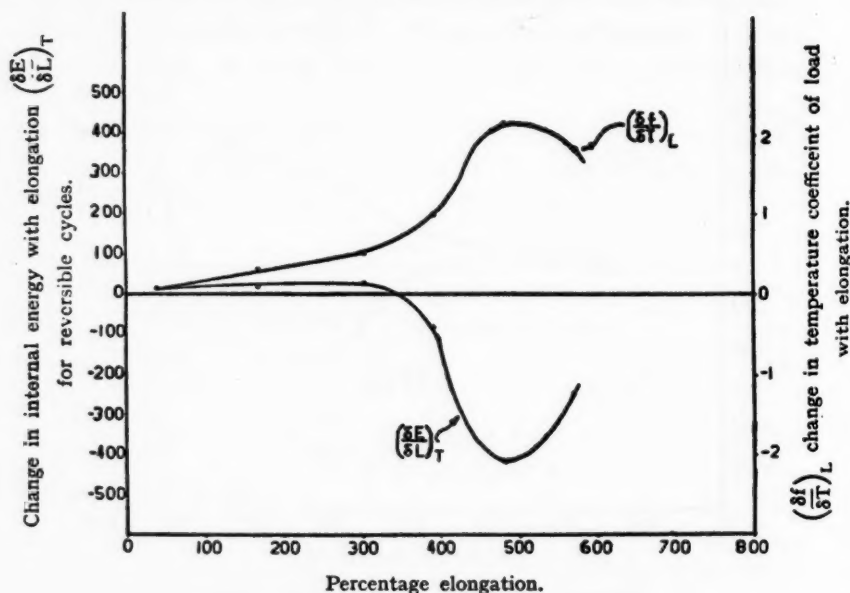


Figure 11— $\left(\frac{\delta f}{\delta T}\right)_L$ and $\left(\frac{\delta E}{\delta L}\right)_T$ for Type T Bands

This too clarifies the theoretical background for the experimental finding that the rubber pendulum can be made to operate only within certain limits of elongation or strain.

This also furnishes direct thermodynamical evidence of changes in the structure of rubber and that these changes begin at a critical stage in elongation.

It is recognized that the experiments here described do not embrace a complete range of cures or a wide range of temperatures, and that the boundaries of the Joule effect region or the region of the heat engine practicability may vary accordingly.

Three Regions of the Rubber Stress-Strain Curve from a Thermodynamical Point of View

Region A; The Steel Spring.—This region (see Fig. 12), extending to approximately 300 per cent elongation for the conditions in the experiments described, is characterized by the comparative absence of heat transfers, relatively complete re-

* The authors desire to express their thanks to R. H. Gerke, Physicist, U. S. Rubber Co., General Laboratories, Passaic, N. J., for making these data available.

versibility or freedom from elastic after-effect; no significant change in internal energy excepting a small positive value, little or no Joule effect, and therefore no availability as a rubber heat engine.

In region A, rubber behaves very much like a steel spring. dQ is virtually zero.

$$dE = -dW = +fdL$$

The work done by the rubber is represented by the decrease in internal energy without thermal phenomena. With no change in internal energy save that due to the potential energy or work done on the band, there would appear to be no change in the inner structure of the rubber.

Region B; The Gas (and the Crystal).—In region B, the region of the Joule effect,

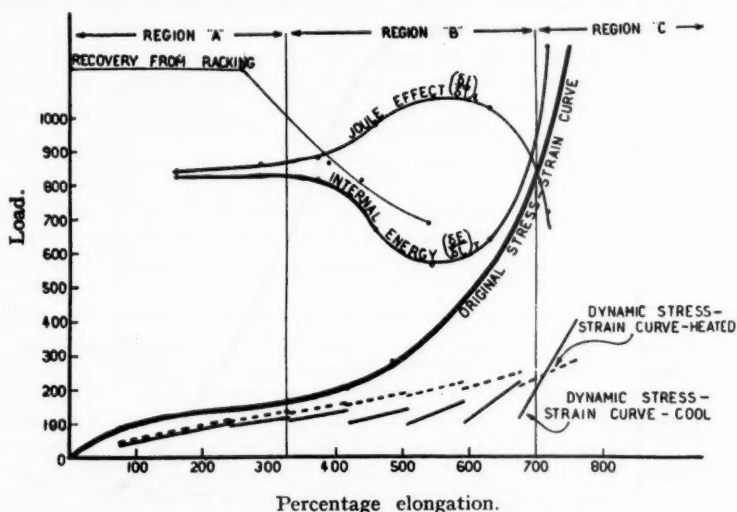


Figure 12—Thermodynamic Analysis of Rubber Stress-Strain Curve

and therefore of the pendulum or other heat engine phenomena, there is the maximum of heat evolution (and, on reversal, of absorption), and $\left(\frac{\delta E}{\delta L}\right)_T$ becomes negative and may become very large in proportion to the other energy transformations. $\left(\frac{\delta f}{\delta T}\right)_L$ reaches its maximum. In this region the stress-strain curve suddenly begins to develop a non-reversible condition (large hysteresis loops). The elements of the dynamic stress-strain curve begin to open up and to be sharply inclined to the extension arm of the stress-strain curve.

Region B is thus suggestive of profound alterations in the internal structure of the rubber.

Region C; The Friction Member.—This region is characterized by the almost entire absence of reversible effects. The Joule effect has disappeared. In this region (see equation 10) the force or tension is deeply influenced by the friction component R . There is no evolution of heat due to decrease in internal energy of state. In this region increased temperature lowers the stress-strain curve by increasing the plastic flow with ultimate failure by slip or rupture. Region C suggests that what ever structural changes have occurred in region B have now been completed. It might be called the region of friction, slip, and failure.

A Guess as to the Structural Changes.—Region B is in some respects similar, from a thermodynamical point of view, to a gas in the sense that the work done is converted into heat, which under suitable conditions may be reversible. If in this region rubber were a perfect analogue of a gas, the total heat evolved would equal the mechanical work done. However, this is not the case, as experiments have shown that the heat evolved in stretching rubber in region B is greater than the work done (Williams, *Ing. End. Chem.*, **21**, 872 (1929)).

The authors incline, in the light of the present data, to consider region B as one in which the development of intense compressional forces in the rubber induced by longitudinal extension brings about the solidification of a phase of oriented or crys-

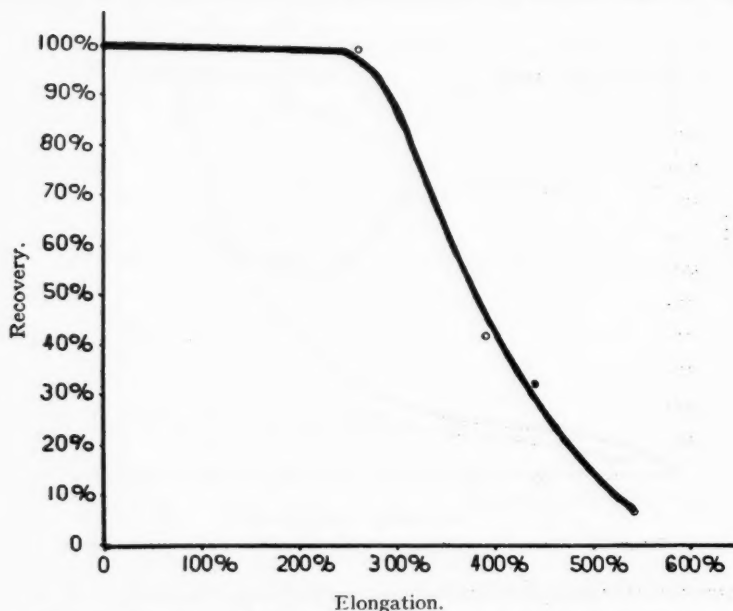


Figure 13—Recovery of Vulcanized Type S Bands when in Contact with Ice

talline nature, accompanied by the evolution of latent heat. If Feuchter's measurements (*Gummi Ztg.*, **29**, 1167 (1925)) indicating that the density of rubber increases on stretching can be accepted as generally valid, the cross-sectional compression forces induced by longitudinal extension would be still more intense. The higher the temperature the greater the lateral compression required to induce this solidification. Note in this connection Figs. 7 and 8. The high temperature specimen began to show the separation of the dynamic stress-strain elements at a higher elongation than did the cool specimen.

The facts also suggest that along with separation through lateral pressure of a solid phase, there remains a viscous liquid phase which, directly solidification begins, disposes itself as thin films which become more or less bound, thus introducing a frictional resistance which accounts for the sudden onset of hysteresis at the beginning of region B.

From this point of view the phenomena in region C are readily pictured. At this point solidification is complete with the exception of exceedingly thin films of vis-

cous liquid serving as a bond between the contiguous elements, fibers or, as many would insist, crystals. The rapid increase in load which is characteristic of region C would be referable to the well-known rigidity of very thin films of such a viscous cementing liquid. The sole effect of higher temperature in region C would then be to cause plastic flow through decreased viscosity of this cement, thus explaining the decreased values for tensiles at rupture obtained and much emphasized by recent investigators (Somerville and Cope, *loc. cit.*). It is suggested that whereas failure at room temperature may be regarded as rupture of the elastic elements, the failure at, for example, 100° C. may be pictured as rather a slippage due to the phenomena mentioned. In any case it is manifest that attention should not be confined to the properties at failure in the case of enhanced temperatures, but extended to include hysteresis and modulus changes at intermediate elongations. Such values might better be determined on the basis of the dynamic stress-strain curve than only upon the extension arm of an initial hysteresis loop.

The Ice Test.—In Fig. 13 is shown the result when one of the soft cured stationers' bands used in the experiments was stretched successively to increasing elongations, placed in the stretched condition on a surface of ordinary ice and allowed to retract. It will be noted that here again at a critical elongation of about 300 per cent the properties suddenly change. For the small elongations the rubber recovered completely. For higher elongations the racking phenomenon became progressively more intensely developed. The higher the state of cure the lower the temperature necessary to bring out this sharp change at the end of region A and the beginning of region B.

At this point attention may be drawn to the elegant application of racking principles to cure estimation of rubber by Gibbons, Gerke, and Tingey (*Ind. Eng. Chem. Anal. Ed.*, 5, 279 (1933)). In this so-called T-50 test, vulcanized rubber is stretched well into region B, frozen at low temperatures, allowed to warm up and the temperature determined at which recovery has reached 50 per cent. An analysis of the above paper confirms the experiments just described. The marked change in the racking properties of these various specimens at the end of region A is clearly shown. It is believed that the conception of a viscous liquid phase, appearing in the form of thin films in a two-phase system, constitutes at least a plausible explanation of this sudden change in thermo-elastic properties.

The Solvent Effect.—It has already been pointed out that the tensional force F' , when allowance is made for non-reversibility, may be expressed as follows:

$$F'' = \left(\frac{\delta E}{\delta L} \right)_T + T \left(\frac{\delta f}{\delta T} \right)_L + R$$

$$F' = \left(\frac{\delta E}{\delta L} \right)_T + T \left(\frac{\delta f}{\delta T} \right)_L - R$$

Where F'' and F' are respectively the non-reversible loads on extension and retraction, $2R$ is then a rough measure of the extent of hysteresis developed. It has been seen (Fig. 4) that a rise in temperature causes a marked decrease in the area of the hysteresis loop which, in terms of the above expression, may be regarded as a decrease in the value of R , the frictional component. Turning now to Fig. 8 it will be noted that, although each cyclic element is of reversible character, there are at least in regions B and C pronounced gaps between these cyclic elements of the stress-strain curve. These may be interpreted as evidence of the fact that the curve as a whole is still non-reversible, even although each element in itself is completely reversible.

The dynamic curve for the warm specimen, as well as lying higher on the paper,

due to the Joule effect, shows no such gaps, because of the effect of higher temperature in reducing viscosity and hysteresis.

On the view that the sudden development of hysteresis at the beginning of region B is due to the solidification of an elastic phase, with the development of thin films of a viscous liquid phase it seemed logical to expect that any agency capable of reducing this viscosity would serve to straighten out or align the dynamic cyclic elements.

In 1919 it was shown (Wiegand, see Whitby's *Plantation Rubber and the Testing of Rubber*, p. 484) that the grain effect of chilled calendered sheets could be eliminated by immersion in a rubber solvent much more readily and quickly than by shrinkage through the application of heat. It was pointed out at that time that the tendency on the part of some writers to ascribe the shrinkage of chilled calendered sheets to the Joule effect could not be considered valid because of the total lack of reversibility of this phenomenon. It is true that chilled calendered sheets like stretched vulcanized rubber, shrink on heating, but it is not true that the shrunk sheets will once more expand on subsequent cooling.

So too, the effect produced by immersion in solvent is clearly not an example of the Joule effect, but rather a viscosity phenomenon. It does not satisfy the requirements of reversibility.

Now, if the presence of a viscous binding liquid between the solid or crystalline elements in stretched vulcanized rubber be assumed, immersion in a solvent should cause retraction in a manner similar to that of the Joule effect, though totally different in origin and mechanism. Such, indeed, was found to be the case. A pronounced retraction of a reversibly stretched vulcanized stationers' band was observed on spraying the specimen with carbon disulfide or other rubber solvent. This effect, which is for the present called the solvent effect, would seem to resemble the Joule effect only to the extent that R , the frictional component in the stress-strain curve, is reduced. The binding effect of the thin films of viscous liquid is reduced through the action of the solvent. This being so, it is clear why, in the case of rubber which has not been previously subjected to successive cycles, the effect of the solvent is to cause not retraction, but further extension. In short, a rubber solvent tends to lower the outward loop of the hysteresis curve and raise the return loop of the curve. On the other hand, the Joule effect, in addition to this, actually raises the curve as seen in Figs. 7 and 8.

In region C the effect of the solvent is similar to that of temperature in that, presumably through increasing viscous flow, the stress-strain curve is lowered, and so also the tensile strength at rupture.

In the literature (Tiltman and Porritt, *India Rubber J.*, **78**, 345 (1929)) the effect of rubber solvents is always stated to be to lower the stress-strain curve of rubber. It is now suggested that this is exactly one-half of the truth. Rubber solvents do lower the outward arm of the first hysteresis loop (and probably also those of a few succeeding loops), but they also raise the retraction arm of the loop. Under conditions where the rubber has been subjected to repeated cycles, stretched rubber will retract under the influence of a solvent. The net result would seem to be that when due regard is paid to the dynamic conditions obtaining in the automobile tire and tube, transmission belt, automotive suspension rubber, etc., experiments designed to expose the effect of temperature changes, softeners, or solvents, should be carried out, not on the extension arm of the first hysteresis loop, but rather on the dynamic stress-strain curve, whether generated in some such manner as that here described, by means of vibration as described by Gerke (*loc. cit.*), or by other equivalent means.

Practical Application of the Solvent Effect.—The pronounced decrease in hysteresis

due to a rubber solvent seems not without practical significance. Rubber articles subjected to severe deformations of rapid frequency would probably develop less heat in the presence of even a small percentage of a solvent, preferably non-volatile. Certain medium gravity petroleum fractions suggest themselves in this connection.

In the case of vulcanized articles which display a residual grain effect, as in the case of some extruded wares, they might be relieved of these residual stresses and strains by treatment with a completely volatile solvent. In short, the retraction of chilled calendered sheets by means of a solvent would now seem to be a phenomenon by no means restricted to raw rubber, and one deserving of further study as a means for minimizing both frictional heat and residual surface strains, which cause early failure in the presence of ozone and sunlight.

In Fig. 12 are shown in diagrammatic form the three regions of the rubber stress-strain curve as pictured on the basis of the data here presented.

Raw Rubber and Vulcanized Rubber.—The work of recent investigators (Clark, *India Rubber World*, 79, 55 (1929); Katz, *Kautschuk*, 5, 6 (1929); Rosbaud and Hauser, *Z. Elektr. Chem. angew. physik. Chem.*, 33, 511 (1927); Hauser and Mark, *Kautschuk*, 3, 228 (1927)) indicates the appearance of an x-ray interference diagram in the case of raw rubber after much less stretching than in the case of vulcanized rubber, or even with freezing (without stretching). In raw rubber the structural elements abound, and on being congealed at low temperatures show crystal patterns. At room temperatures even a small degree of lateral compression (longitudinal extension) would be expected to precipitate or congeal these elements in large numbers with concomitant development of thin films of the second phase which is commonly assumed to be a liquid. After the rubber has been milled and vulcanized, greater stretch or lateral compression would be required to precipitate out the solid phase to an extent sufficient to develop the thin films of bound liquid phase.

The structural hypothesis here mentioned is recognized as tentative and incomplete. A more highly developed picture is needed to explain the known facts of x-ray analysis. It is also possible that those who, like Boggs (*Ind. Eng. Chem.*, 22, 748 (1930)), look upon soft vulcanized rubber as a mixture of a pure vulcanized substance with uncured material, will prefer to discuss these characteristic regions of the curve in terms of these components and their properties.

At all events the methods of analysis here presented may perhaps serve to fix ideas and to furnish objective, and even quantitative criteria, by which the approach of any given specimen to the condition of perfect elasticity may be evaluated.

Of those who would fain believe they have produced pure soft vulcanized rubber it must be asked: First, have they extended the reversible characteristics of region A to regions B and C? Secondly, have they eliminated the solvent effect? Thirdly, does the dynamic stress-strain curve coincide with the initial extension curve? Fourthly, have racking phenomena become the same for all elongations? Fifthly, does the Joule effect extend through region C, that is up to the point of rupture?

The first to produce such a rubber will inaugurate a new era in the science of rubber.

Summary

(1) The rubber pendulum, as an example of a reciprocating rubber heat engine for the conversion of heat into useful work by means of Carnot's cycle, with rubber functioning by virtue of the Joule effect as the thermal substance, has been described in detail.

(2) Initial variations in the period of the pendulum are caused by, and so serve as accurate measures of, the fatigue or elastic after-effect of vulcanized rubber.

(3) The early attainment of a constancy in the period of oscillation indicates that at least for cyclic elongations of slightly under 100 per cent conditions of reversibility can be obtained both for slightly undercured and well cured pure gum stationers' bands.

(4) With such attainment of reversibility, the application of the second law relationships to the thermo-elastic changes involved in pendulum operation has made possible a thermodynamical study of energy transformation for successions of cyclic elongations taken at intervals along the stress-strain curve of these rubber specimens.

(5) From this analysis the change in internal energy per unit extension has been determined at various points along the stress-strain curve. This value was found positive up to about 350 per cent elongation, thereafter strongly negative to about 675 per cent elongation, and thereafter once again positive.

(6) These variations furnish thermodynamical evidence of important changes in the rubber structure with progressive elongations. The three respective regions of the rubber stress-strain curve have therefore been tentatively called region A, B, and C. In region A, rubber behaves thermodynamically like a steel spring, with negligible hysteresis and thermal effects. In region B, like a gas combined with strongly exothermal structural changes involving also a sharp increase in hysteresis. In region C the rubber behaves thermodynamically like a friction member, involving disappearance of reversible heat transfers.

(7) The Joule effect and therefore the capacity of vulcanized rubber to actuate a rubber heat engine is confined to region B.

(8) The three regions, A, B, and C, thus derived on thermodynamical grounds, correspond also to changes in other physical properties. In particular, it is pointed out that the ability to rack vulcanized rubber undergoes a sharp increase in passing from region A to B.

(9) The stress-strain curve obtained by a succession of strictly reversible cyclic elongations is called the dynamic stress-strain curve. The component elements of this curve begin to separate sharply in passing from region A to B.

(10) The effect of increased temperature on the dynamic stress-strain curve is two-fold, first to raise it, which is the Joule effect; and, second, to straighten it, which may be regarded as a thermo-plastic effect.

(11) The effect of rubber solvents on the retraction of chilled calendered sheets has been shown to extend to vulcanized rubber and under pre-worked conditions causes a retraction similar to the Joule effect, but entirely different in origin. This has been tentatively called the solvent effect.

(12) Statements in the literature that the effect of solvents is to lower the stress-strain curve of rubber are shown to be valid only for the extension arm of an early hysteresis loop. The true effect of a rubber solvent is to narrow the hysteresis loop. In region C the effect of solvent, like that of raised temperature, is to increase plastic flow and thus to depress tensile values at, and close to rupture.

(13) The practical significance of the solvent effect, both in reducing heat development in rubber subjected to rapid deformation and in relieving residual stress in cured rubber, is pointed out.

(14) From the experimental studies made, the authors put forward the tentative structural hypothesis that at the beginning of region B, a point which will, of course, vary depending on the state of cure, of combined sulfur, and of the temperature of the rubber specimen, the increase in lateral compression causes the precipitation of a solid phase with the simultaneous development of thin films of viscous liquid which become increasingly bound as the extension, that is to say the lateral compression, of the rubber specimen increases. At the end of region B such precipita-

tion has reached substantial completion, the thin films of bound liquid now completely freeze together the solid or crystal elements, extensibility has reached its limit, and rupture occurs.

The effect of higher temperatures or of solvents in region C is to melt or dissolve this bound liquid phase, thus resulting in plastic flow with lowered physical properties at rupture.

(15) The study of the effect of higher temperatures or of solvents upon the properties of vulcanized rubber should not be confined either to values at rupture or to the extension arm of the rubber curve. Their effect upon the dynamic stress-strain curve as here described would seem to furnish a more accurate picture of the role they play in actual service.

Studies on the Joule Effect in Rubber

I. The Thermal Effect on Stretched Vulcanized Rubber

Yoshio Tanaka, Shū Kambara, and Hironosuke Fujita

TECHNICAL CHEMICAL LABORATORY, TOKYO KOGYO DAIGAKU, TOKYO UNIVERSITY COLLEGE OF TECHNOLOGY

The Joule effect is an interesting problem to rubber scientists, but on account of experimental difficulties, few papers on this problem have been reported. This paper is a result of a series of experiments on the elongation and shrinkage of stretched vulcanized rubber when heated and cooled.

Experimental

Ring-shaped specimens, 10 mm. in inside diameter, 1 mm. thick, and 17 mm. wide, were used throughout the tests. The specimen was placed in an air thermostat ($20 \pm 0.5^\circ \text{C.}$) and stretched by a weight of 3 kg. which was connected to the specimen through a wire rope. The elongation of the specimen under this tension was measured by an attached scale, and the ratio of the elongated length to the original length is noted as "*E*" (elongation) in the following tables. Under this stretched condition, the specimen was heated by another water thermostat at 80°C. constant within 0.5°C. By this heating, the specimen elongated a little. This elongation, shown by the ratio to the original length, is noted as "*HE*," i. e., the heating elongation. The water thermostat was then taken away, and the specimen cooled to the temperature of the air thermostat, i. e., 20°C. In this time, a considerable elongation was observed. When the specimen was heated to 80°C. again by the water thermostat, a shrinkage comparable to the previous elongation appeared. Thus, the first heating results in an irreversible elongation, after which the successive cooling and heating show a reversible elongation and a shrinkage, respectively. These thermal effects may be assumed to represent the Joule effect. The term "*J*" in the following tables is the ratio of the second elongated length (with the heating bath removed) to the original length.

The irreversible elongation by the first heating is a peculiar phenomenon which has never been reported in the literature. This phenomenon seems to be caused by the internal stress of fresh vulcanized rubber, such as the calender effect.

Experiment A, Influence of Time of Cure.—One hundred parts of pale crepe rubber masticated for 10 minutes were mixed with 5 parts of sulfur and vulcanized in a hydraulic press for various periods at a steam pressure of 60 lbs. per sq. in. After storage for at least 24 hours, the specimen was stretched on the apparatus above described and subjected to the temperature change described.

Time of Cure (Min.)	<i>E</i> (%)	<i>HE</i> (%)	<i>J</i> (%)
40	1122.7	115.2	28.9
50	1041.7	86.2	41.1
60	1012.7	64.8	48.0
80	925.9	9.8	75.2
100	931.7	-1.2	97.2

Experiment B, Influence of Sulfur Content.—One hundred parts of pale crepe rubber were masticated for 10 minutes, and mixed with 4, 5, 6, 7, and 9 parts of

sulfur. Each batch was vulcanized for 60 minutes at a steam pressure of 60 lbs. per sq. in. After this, the specimens were analyzed to determine the combined and free sulfur contents.

Amount of Sulfur Mixed (Parts)	Total S (%)	Free S (%)	Comb. S (%)	E (%)	HE (%)	J (%)
9	8.52	4.62	3.90	601.8	-1.7	78.1
7	5.80	3.22	2.58	885.3	92.6	78.1
6	5.43	2.97	2.46	914.3	101.3	74.1
5	4.22	2.50	1.72	980.6	130.2	53.2
4	3.63	2.18	1.45	1122.7	158.0	38.2

Experiment C, Influence of an Organic Accelerator.—Pale crepe rubber 100, sulfur 5, and diphenylguanidine 0.5 were mixed and vulcanized for various periods as in Experiment A.

Time of Cure (Min.)	E (%)	HE (%)	J (%)
10	960.6	240.7	2.3
15	914.3	166.7	63.7
20	781.2	82.2	99.5
30	694.4	16.8	155.1
40	630.8	-4.6	129.1

Experiment D, Influence of Mastication.—Pale crepe rubber was masticated for various periods, viz., 5, 10, 20, 30, and 50 minutes. In 100 parts of the masticated rubber were mixed 5 parts of sulfur and the mixture was vulcanized for 80 minutes at a steam pressure of 60 lbs. per sq. in.

Time of Mastication (Min.)	E (%)	HE (%)	J (%)
5	879.6	-2.3	114.0
10	816.0	-1.2	86.8
20	839.1	2.9	115.7
30	885.4	4.1	104.7
50	902.8	44.0	95.5

Experiment E, Influence of Ultra-Violet Rays.—The standard specimens used in Experiment A were exposed to ultra-violet radiation of a mercury vapor lamp in open air for various periods.

Time of Exposure (Hrs.)	E (%)	HE (%)	J (%)
2.5	966.4	108.8	85.6
5.0	983.8	123.8	88.0
7.5	989.6	124.4	83.3
10.0	995.3	126.2	73.5

Experiment F, Influence of Filler.—One hundred parts of pale crepe rubber were masticated for 10 minutes, and were then mixed with 5 parts of sulfur and various parts of carbon black. Each batch was vulcanized for 60 minutes at 60 lbs. per sq. in. steam pressure.

Content of Carbon Black (Parts)	E (%)	HE (%)	J (%)
5	752.3	75.8	68.3
10	601.8	94.3	50.9
15	532.4	110.5	37.0
20	474.5	144.7	26.0

Summary and Conclusion

The experiments may be summarized as follows:

1. With an increase in the time of cure, the elongation and heating elongation diminish and the Joule effect increases.
2. An increase in the vulcanization coefficient is followed by a decrease in the elongation and heating elongation and an increase in the Joule effect. The increase in the Joule effect, however, has a limit.
3. An organic accelerator reduces the elongation and heating elongation and increases the Joule effect.
4. The greater the degree of mastication the greater the elongation and the heating elongation and the less the Joule effect.
5. By exposure to ultra-violet radiation, the elongation and heating elongation are increased and the Joule effect decreased.
6. A filler increases the heating elongation and decreases the elongation and the Joule effect.

Thus samples with relatively high elongations at a definite tension have relatively high heating elongations and low Joule effects. Such specimens seem to have been affected by the disaggregation and depolymerization of the rubber molecules. The effects of the time of cure, mastication, and exposure to ultra-violet radiation prove this fact. Vulcanization increases the Joule effect, but on the other hand, it is accompanied by a disaggregation and depolymerization of the rubber molecules, so the increase in the Joule effect with the progress of vulcanization has a limit. On vulcanization with an accelerator, the combination of sulfur occurs so rapidly that the increase in the Joule effect is predominant. A filler, such as carbon black, behaves only as a diluent of Joule effect. These results lead to the conclusion that the more highly polymerized rubber molecules and their sulfur compounds seem to be the chief factor in the Joule effect of vulcanized rubber.

An Investigation of the Visco-elastic Properties of Rubber

J. C. Eccles (Fellow of Exeter College, Oxford) and J. H. C. Thompson (Fellow of Merton College, Oxford)

1—Introduction

The object of the present investigation is to examine the dynamical properties of rubber in the light of the theory of *visco-elasticity*. This theory, which attempts to describe the dynamical behavior of deformable solids, has been deduced from the thermodynamics of a solid with the help of certain physical assumptions.¹ Certain mathematical approximations are also necessary to obtain the stress-strain relations in simple form. In this form they express each stress component as the sum of two groups of terms, the first being the usual Hooke's Law expression, linear in the strain components, while the second is a similar expression in terms of the *rate of strain* components. Now, according to the theoretical deduction of these stress-strain relations, it is not to be expected that they will be of universal applicability, least of all for a substance which has so many queer elastic properties as rubber. But the theory suggests that, between suitably defined *upper and lower visco-elastic limits* for the rate of strain,² these stress-strain relations may still be capable of describing approximately the dynamical behavior of a substance such as rubber.

The damping of vibrations in solids has been a subject of frequent investigation, and certain visco-elastic constants for metals at various temperatures have already been determined.³ But investigators, who have noticed deviations from theoretically predicted results, have either attributed these deviations to experimental errors,⁴ or else pointed out simply that the visco-elastic hypothesis fails and must be modified in some way.⁵ Often this latter point is clear from theoretical considerations alone—for instance, rubber shows a residual creep after being strained, which is contrary to the assumptions of the theory of visco-elasticity. But, just as in the statics of deformable solids our first interest is in the behavior within the elastic limits, in the dynamics of deformable solids our first interest is in the behavior within the visco-elastic limits. In the present investigation we attempt to discover within what limits, if any, the theory of visco-elasticity is applicable; and then to determine the values of the "normal visco-elastic constant" and the "coefficient of normal viscosity" within those limits.

The experiments present two unusual features. The forced vibrations of the system are of a high frequency (originally 135 per second; later the apparatus was modified to give any frequency between 135 and 16 per second), while the maximum deviation of the strain in the rubber from that in the equilibrium position of the system never exceeds 0.002. This latter fact is of great importance. Iokibe and Sakai (*loc. cit.*) found that the damping of the vibrations of torsional pendulums was dependent on the amplitude of vibration, and obtained the "true" damping by interpolation; and fatigue effects in metal wires, noticed by Lord Kelvin (*loc. cit.*), have been shown by Thompson⁶ to be due to excessive straining.

2—The Apparatus

Fig. 1 shows the essential features of the oscillating torsion system, by means of

which forced longitudinal vibrations are set up in the rubber cylinders. A is a light but rigid steel lever arm, 12 cm. long, which is firmly welded at its center perpendicular to the free end of the torsion rod B. This rod is made of hard steel; its main shaft has a diameter of 1.85 mm. and a length of 3.3 cm. It terminates at one end in a cylindrical expansion, so that this may be rigidly fixed by a screw in the brass block J. At the other end, just beyond the attachment of the lever arm, there is also a cylindrical expansion C, but at its center it has been ground down to produce an axial knife-edge, which rests freely on the flat edge of the fixed plate E. Beyond C the steel mirror F is fixed to the narrow continuation of the torsion rod. The plate E is fixed to the supporting bar G by the brass block H, and the brass block J is a continuation of H. The brass bar G is in turn firmly attached to a rigid supporting system, consisting of a steel girder framework strained down to a steel column fixed in concrete.

The strip of soft iron K at one end of the lever arm serves to support the weighted

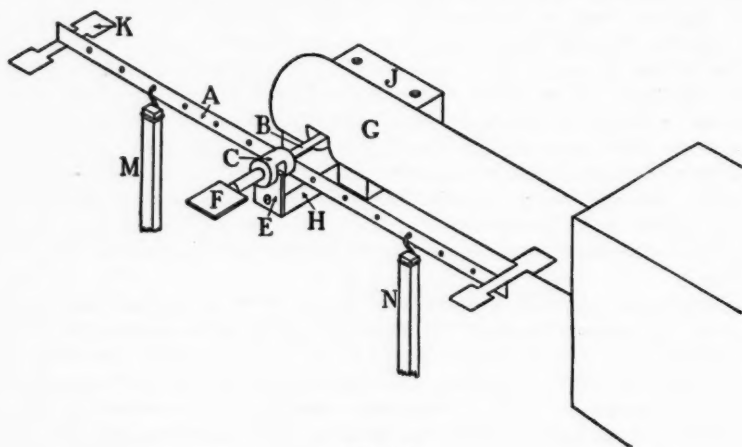


Figure 1

electromagnet which is used to set the system into vibration. The similar strip at the other end restores the symmetry of the vibrating system about the axis of the torsion rod. Great care has been taken to construct the moving parts so that they are completely symmetrical about the axis of the torsion rod, which is the axis of vibration. In this way all "chatter" at the knife-edge has been avoided.

Equal rubber cylinders M and N are attached to the lever arm by short steel hooks passing through corresponding holes on opposite sides of the lever arm. A knife-edge on the hook rests in a V-shaped groove cut in the hole, the other end of the hook being tied to the rubber. The lower ends of the vertical rubber cylinders are gripped by clamps which are attached to the cast-iron top of a heavy table. The unstretched lengths of the rubber cylinders are equal, as are the distances of the holes of attachment from the axis of torsion. The symmetry about the axis is thus maintained. When the system is set into its equilibrium position just before an experiment the rubber cylinders are adjusted to equal tensions (of the order of 100 grams weight).

An optical system has been used in recording the vibrations of the system. Light from a 500-c.p. pointolite lamp is concentrated by a condenser on to a narrow

perpendicular slit; and beyond this a lens is placed so as to form an image of this slit on the horizontal slit of a falling plate camera. On the way to the camera, however, the beam of light is reflected downwards on to the horizontal mirror F, from which it is again reflected upwards. Finally another prism restores the beam to its original path towards the camera slit, where it appears as a perpendicular bright line. Since the axis of torsion is parallel to the original direction of the beam of light, any torsional movement of the system produces a corresponding lateral movement of the perpendicular image across the camera slit. The torsional displacements are always small (less than 2°), so they are proportional to the lateral displacements of the image. The constant of proportionality is easily calculated.

In order to set the system into vibration a torsion is produced by attaching a weighted electromagnet to the under surface of K. The falling plate of the camera breaks the circuit through the electromagnet, which falls clear, releasing the lever arm. A graph of the subsequent vibrations is thus obtained on the photographic plate. The length along the direction of fall of the plate is proportional to the time as the plate falls uniformly, though to ensure accuracy the time is measured by the vibrations of a standard tuning fork, superimposed on the plate. The lateral displacement on the plate is, of course, proportional to the torsional displacement of the lever arm.

Various constants of the apparatus are capable of alteration. The distance of the points of attachment of the rubber cylinders from the axis can be varied from 0.505 cm. to 5.04 cm. in steps of approximately 0.5 cm. Brass riders, screwed on to the lever arm, have been used to vary the period of vibration of the torsional system. In this way it can be varied from 0.736×10^{-2} to 6.16×10^{-2} seconds. The brass riders are identical, but care has to be taken to fix them at equal distances from the axis of torsion in order to maintain the symmetry of the system about this axis.

3—The Analysis of the Experiment

The experimental results are contained in the photographic record of the angular displacement of the lever arm plotted against the time. The quantities most easily measured are the successive amplitudes and periods of vibration. The object of the analysis is, in the first place, to predict the form of this graph on the assumption that the rubber cylinders are visco-elastic; and, further, to obtain an expression for the normal visco-elastic constant of rubber in terms of these amplitudes and periods of vibration.

It cannot be assumed that the rubber cylinders are always uniformly strained throughout their length. For, in some of the experiments at least, the period of free longitudinal vibrations in the rubber cylinders and the period of vibration of the torsional system are of the same order of magnitude. Thus the analysis is essentially the determination of the forced longitudinal vibrations in the rubber cylinders M and N, subject to fixed end conditions at their lower ends, and to the conditions of the continuity of the motion of their upper ends with the motion of the lever arm.

4—Experimental Results and Calculations

The results of two sets of experiments are given here. A preliminary set of experiments gave a very wide range of values for τ —from 3.12×10^{-4} to 18.0×10^{-4} seconds, while in addition the logarithmic decrement was not quite constant throughout individual experiments. These queer results are probably due to the fact that the frequencies of vibration were too high to permit the use of the approximations (3.5) and (3.6). (The frequencies of vibration per second ranged from

136 to 32, the former being of the same order as $1/\tau$, which was later found to be about 348 sec.⁻¹.) Ordinary catapult elastic was used in these preliminary experiments.

Experiments I.—This set of experiments is a natural sequel to the preliminary set, differing only in the fact that the frequency of vibration was almost halved by the addition of extra brass riders on the lever arm, in order to make the analysis of the experiment applicable. Again ordinary catapult elastic was used. Three experiments were performed with the rubber cylinders attached at distances 0.505, 1.505, and 3.01 cm., respectively, from the axis. The tension in the rubber in the equilibrium position was 100 gm. weight.

In the first experiment the photograph of the vibration was exactly as predicted by theory. After two or three initial logarithmic decrements as high as 0.003, the logarithmic decrement did not vary from 0.00223 outside the limits of error in measurement. (The amplitudes and periods of vibration were measured from the photographic plates by placing them over accurate millimeter squared graph paper. In this way it is possible to measure to 0.1 mm. In this series of experiments, errors of measurement cannot cause an error of more than 3 per cent in the calculated value of τ .) The period also was constant, as predicted by the theory.

But in the second and third experiments, after initially high logarithmic decrements, the logarithmic decrements were not constant, but increased as the amplitude decreased—in the last experiment by as much as 36 per cent. This immediately suggests that these experiments are carried out in the region of the upper visco-elastic limit for the rate of strain;⁷ for, since the period and the initial torsional amplitude are roughly the same in the three experiments, the rate of strain is greatest when the rubber cylinders are attached at the points most distant from the axis. (The question of the approximations (3.5) and (3.6) does not arise, as the frequency is roughly the same in the three experiments.) If the variation of the logarithmic decrement is due to this cause, then the values of τ calculated at various instants in the three experiments should be consistent when plotted against the average rate of strain (measured by the change of strain per vibration divided by the period of vibration).

TABLE I
CATAPULT ELASTIC. $T_0 = 5.76 \times 10^{-2}$ SECONDS; $L_0 = 0.00019$

Expt.	Length of Lever Arm, a in Cm.	Period T , in 10^{-2} Sec.	Amplitude of Vibration on Photograph in Cm.	Observed Logarithmic Decrement L	Logarithmic Decrement Calculated for $\tau = 28.7 \times 10^{-4}$ ($E' = 3.42 \times 10^4$)	$\tau \times 10^4$ Calculated from Observed L	$E' \times 10^{-4}$ Calculated from Observed L	Average Rate of Strain (in Sec. ⁻¹)
I. 1	0.505	5.75	2.20	0.00220	0.00223	28.3	3.37	0.052
			1.32	0.00228		29.5	3.51	0.031
			0.96	0.00218		28.1	3.34	0.023
			0.75	0.00224		28.9	3.44	0.017
			2.67	0.0163		26.8	3.19	0.190
I. 2	1.505	5.68	1.50	0.0172	0.0175	28.3	3.37	0.106
			1.00	0.0176		28.9	3.44	0.071
			0.77	0.0180		29.6	3.52	0.055
			1.70	0.050		21.0	2.50	0.312
			1.19	0.056		23.5	2.80	0.221
I. 3	3.01	5.10	0.70	0.060	0.068	25.2	3.00	0.129
			0.30	0.068		28.5	3.39	0.055

The value of τ calculated from the experimental results is
 $\tau = 28.7 \times 10^{-4}$ sec.

The normal coefficient of viscosity is thus

$$E' = 3.42 \times 10^4 \text{ dyne sec. per sq. cm.}$$

Experiments II.—A second and more extensive set of experiments was performed, using pure black rubber cylinders. The object was not only to determine τ for pure rubber, but also to investigate the damping of vibrations over a wider range of frequencies. Since pure rubber is much less viscous than ordinary catapult elastic, τ is less, and consequently the analysis of the experiment is valid for vibrations of higher frequency. Lower frequencies could not be obtained with the apparatus, whereas higher frequencies had already been used in the preliminary experiments. The lengths of the rubber cylinders were almost doubled in an attempt to reach the lower visco-elastic limit.

Unfortunately the apparatus is essentially designed for the study of very viscous solids, and when the logarithmic decrement of the damped vibrations is less than ten times the logarithmic decrement of the free vibrations, the photographs seem to be very irregular. Small periodical fluctuations of the logarithmic decrement had already been noticed in Experiments I, but they were small and were "smoothed out" without difficulty. But in the second series of experiments, when the rubber cylinders were attached close to the axis in the slower vibrations, the logarithmic decrements were small and these fluctuations play a dominant role. They appear to be due to vibrations set up in the lever arm, which is heavily loaded with brass riders, but it has not been found possible to obtain an exact theory of the fluctuations and so eliminate them. The experiments with $a = 0.505$ cm. were abandoned. The results and calculations of the remaining experiments are given in Table II. Even in these experiments the photographs do not justify an examination of the damping from one vibration to the next. Accordingly the logarithmic decrements given in the table are averaged values. It is of interest to note, however, that the logarithmic decrements showed no tendency to increase with decreasing amplitude (and consequently decreasing rate of strain) in the first two experiments, where this would have been observable.

TABLE II
PURE BLACK RUBBER

Expt.	$T_0 \times 10^2$	L_0	a	$T \times 10^2$	L'		L		$\tau \times 10^4 E' \times 10^{-4}$ (Calculated from Observed L')		Average Rate of Strain
					300 G. Tension	150 G. Tension	300 G. Tension	150 G. Tension	Observed	Observed	
II.1.a	3.67	0.0002	5.04	3.00	0.0222	0.0261	3.6	0.47	0.5	to 0.15	
II.1.c	3.67	0.0002	1.01	3.56	(?)	0.0016	4.4	0.57	0.09	to 0.03	
II.2.a	4.75	0.0005	5.04	4.10	0.0217	0.0219	4.2	0.55	0.36	to 0.12	
II.2.b	4.75	0.0005	2.02	4.59	0.0055	0.0054	5.4	0.70	0.14	to 0.04	
II.2.c	4.75	0.0005	1.01	4.66	(?)	0.0020	6.1	0.79	0.07	to 0.02	
II.3.b	6.16	0.0003	2.02	6.04	0.0048	0.0048	6.1	0.79	0.10	to 0.02	

It is difficult to draw any definite conclusions from these results on account of the absence of a detailed analysis of the individual experiments, but the results suggest a probable value for τ for pure rubber to be

$$\tau = 6 \times 10^{-4} \text{ seconds}$$

with the upper visco-elastic limit for the rate of strain approximately 0.1 per second as for catapult elastic. A glance at Table II shows that the only experiment which is inconsistent with the conclusion is II.1.c, where the logarithmic decrement is so small as to be subject to considerable error in measurement.

The corresponding value of the coefficient of normal viscosity is

$$E' = 0.78 \times 10^4 \text{ dynes-sec. per sq. cm.}$$

It is of interest to note that no fatigue effects were detected in either series of experiments. Care was taken not to keep the rubber stretched except for the brief duration of the actual experiment; but, after each set of experiments, the first experiment was carried out again, without giving observably different results.

We are indebted to Professor E. A. Milne for some helpful suggestions, particularly in the early stages of the work.

Summary

An account is given of an investigation of the visco-elastic properties of rubber by means of observations on the damping of forced longitudinal vibrations. An attempt is made to determine the visco-elastic limits for rubber, as well as the normal visco-elastic constant τ and the coefficient of normal viscosity E' . The analysis of the experiment predicts the form of the photographic record of the damped vibrations, and gives an expression for τ in terms of the period of vibration and the logarithmic decrement of the amplitude per vibration. Two series of experiments are described in detail.

In the first series, where catapult elastic was used, the experimental results are susceptible of detailed analysis. They agree with those predicted by the theory of visco-elasticity when the rate of strain does not exceed 0.1 per second. This is the upper visco-elastic limit. The lower visco-elastic limit for the rate of strain was not reached, so it must be less than 0.017 per second. The value obtained for τ is 28.7×10^{-4} seconds, and the corresponding value of E' is 3.42×10^4 in c.g.s. units.

In the second series of experiments pure black rubber was used, and a wider range of frequency of vibration and rate of strain was obtained. Also experiments were carried out at different mean tensions. The experimental results show signs of some unknown disturbance and are difficult to analyze. They suggest 6×10^{-4} seconds as a probable value for τ , and 0.78×10^4 for E' , for pure black rubber, with a rate of strain 0.1 per second as a probable upper visco-elastic limit (at a mean tension of 150 grams weight). The value of τ at 300 grams mean tension does not differ significantly from that at 150 grams.

References

- ¹ Thompson, *Phil. Trans.*, Series A, **231**, 339 (1933).
- ² See Thompson (*loc. cit.*), pp. 360, 406. The upper visco-elastic limit represents the limit imposed by the mathematical approximations; the lower limit is imposed by the physical assumptions (neglect of plasticity).
- ³ Honda and Konno, *Phil. Mag.*, **42**, 115 (1921).
- ⁴ E. g., Iokibe and Sakai, *Ibid.*, **42**, 397 (1921).
- ⁵ E. g., Thompson (Lord Kelvin), *Proc. Roy. Soc.*, **14**, 289 (1865); Voigt, *Ann. Physik*, **47**, 671 (1892).
- ⁶ *Phys. Rev.*, **8**, 141 (1899).
- ⁷ The theory of visco-elasticity is limited by the upper visco-elastic limit because, in the general theory, the expansion of the dissipation function as a quadratic function of the rate of strain components is only permissible if they are less than a certain value. This value is the upper visco-elastic limit. See J. H. C. Thompson (*loc. cit.*), pp. 359-360.

Photoelastic Properties of Soft, Vulcanized Rubber

Wilfred E. Thibodeau and Archibald T. McPherson

1. Introduction

This paper describes an exploratory study of the photoelastic properties of transparent, soft, vulcanized rubber. The work was originally undertaken to obtain data on rubber samples that were used in an investigation of stresses in models by the photoelastic method,¹ and was extended to provide general information on the relation of the photoelastic properties to the composition of rubber.

Measurements of the photoelastic behavior of rubber have been made by several previous investigators, whose work points to a functional relation between double-refraction and stress. Bjerken² made measurements on rubber of unspecified composition at stresses from 5 to 69 bars, which corresponded to elongations from 66 to 434 per cent. Rossi³ observed the behavior of three types of rubber compositions, (1) crude rubber, (2) the same mixed with oil and wax, and (3) rubber vulcanized with 15 per cent of sulfur and subsequently extracted with benzene. Rossi's measurements extended only to stresses of 5 to 7 bars, which corresponded to elongations of 50 to 100 per cent. The measurements of the coefficient of relative retardation by both Bjerken and Rossi, when plotted as functions of stress, give smooth curves which are either linear or nearly so. Van Geel and Eymers,⁴ however, working with sheets of rubber made by the evaporation of latex, obtained a discontinuous relation between relative retardation and stress. Other investigators have studied the double-refraction of rubber in relation to the structure. This latter work is summarized in a recent paper by Rowland.⁵

The contribution of the present investigation lies in the fact that it presents measurements made over relatively wide ranges of stress and composition, and indicates that for any given rubber compound the relation between relative retardation for unit thickness and stress can be expressed by a simple equation. For certain compounds made with organic accelerators the relation may be simplified to a linear one, while for rubber-sulfur compounds the relation is a function of the combined sulfur content.

The present investigation leaves untouched a number of factors which may have important bearing on the photoelastic behavior of rubber. The measurements were all made at approximately the same temperature, that of the room, and with light of one wave-length, the green line of mercury. The results obtained represent the behavior of rubber samples being stressed for the first time, and under conditions which produced no appreciable optical creep.

The definitions, symbols, conventions, and literature on photoelasticity up to 1931 are to be found in a recent comprehensive text on the subject by E. G. Coker and L. N. G. Filon, entitled "A Treatise on Photoelasticity," Cambridge University Press (1931).

2. Preparation of Specimens

The specimens for photoelastic measurement were made from three types of rubber compounds. Compounds of the simplest type were prepared from rubber

TABLE I
COMPOSITION OF SAMPLES

Composition and Treatment Components (parts by weight):	A	B	C	D	E	F	G	H	I	J	K	L	M
Pale crepe rubber	100	100	100	100	100	100	100	100	100	100	96	94	92
Rubber hydrocarbon	1	1	1	1	1	1	...	1
Zinc oxide (Kadox)	1	1	1	1	1	1	1	1	1	1
Stearic acid	1	1	1	1	1	1	1	1	1	1
Tetramethylthiuram di- sulfide	0.5	0.3	0.3
Mercaptobenzothiazole	1	0.5	0.5
Sulfur	0.3	2	4	2.5	4	3	4	5	6	7	4	6	8
Selenium	0.5
Conditions of vulcanization:													
Time (min.)	45	30	40	60	60	300	300	300	300	300
Temperature (°C.)	134	126	126	134	134	148	148	148	148	148
Composition:													
Free sulfur, per cent	...	0.10	1.28	1.06	1.38	0.04	0.05	0.09	0.08	0.08
Combined sulfur, per cent	...	2.05	2.40	1.60	2.46	2.85	3.69	4.65	5.35	6.19

* The preparation and composition of these samples are discussed in the paper cited in footnote 6.

hydrocarbon and sulfur, and were vulcanized so as to bring practically all of the sulfur into combination with the rubber. These are represented in Table I by formulas *K*, *L*, and *M*, which were prepared in connection with an investigation on the chemical properties of rubber.⁶ Compounds of another type were made from crude rubber and sulfur, together with small amounts of zinc oxide and stearic acid; the two latter ingredients were introduced to render these compounds more nearly comparable to those of the third type in which accelerators were employed. The compounds made from crude rubber and sulfur are represented by formulas *F* to *J*, inclusive, and the compounds made with accelerators, by formulas *A* to *E*, inclusive. The accelerators employed were tetramethylthiuram disulfide and mercaptobenzothiazole, each with two different percentages of sulfur. One additional compound, *A*, was made using a combination of the two accelerators and a small percentage each of sulfur and selenium.

The specimens were prepared in the familiar dumb-bell shape commonly used for tensile tests. The thinner specimens were cut with a die from molded sheets, but in the case of thicker specimens the preparation in this manner resulted in curved edges, so recourse was had to molding and vulcanizing such samples in the desired form. The molds consisted of frames provided with sheets of polished aluminum for covers. In making samples, an excess of stock was placed in a mold which was pressed between the platens of a vulcanizing press at a temperature of about 100° C. All stock which overflowed was carefully removed and the mold then placed in a press at the requisite temperature for vulcanization. The specimens so prepared were uniform in thickness to a high degree. Fine reference lines were printed on the specimens at the time of vulcanization by ruling scratches on the aluminum sheets used for covering the mold, and filling these scratches with carbon black.

Specimens from 0.7 to 2.7 mm. in thickness were employed. The constricted portion of the specimens was about 6.5 mm. in width; the length between the reference marks was about 50 mm.

3. Apparatus and Experimental Procedure

The experimental observations which were made included the determination of the dimensions of the specimens, both in the unstressed and in the stressed condition, and the measurement of the relative retardation of the light vibrations respectively parallel and perpendicular to the direction of stress in the specimens.

The thickness and the width of samples in the unstressed state were measured by means of screw micrometer gages⁷ which were thought to be reliable to about 0.0002 inch or 0.005 mm. Measurements of the length of rubber specimens, both before and during the application of stress, were made by means of an improvised cathetometer which operated with a precision of about 0.2 mm.

A few direct measurements of the thickness and the width of specimens under stress were made with the screw-micrometer gage, but in most instances these dimensions were computed from the original thickness and width, and the elongation, as will be discussed in a subsequent part of this paper.

The relative retardation, or the distance by which the extraordinary or slow wave lags behind the ordinary wave in passing through the sample under stress was measured by means of the well-known Babinet compensator. The optical system consisted of a light source, a polarizing nicol furnishing light vibrating at 45 degrees to the direction of stress, the compensator, the sample under stress, an analyzing nicol at a position of extinction relative to the polarizer, together with a ground-glass screen and accessory projection components. The light source was a mercury arc

from which light of wave-length 5461 A. U. was isolated by the use of an optical filter. The compensator had an aperture about 3 cm. square. Its range was 11 bands, 0.479 cm. apart, so the constant was $5461/0.479$ or 11,400 A. U. per cm. The position of a band could be read to about 0.01 wave-length.

The procedure in making stress-optical measurements was the following: A sample on which measurements of dimensions had been made was mounted between the crossed nicols; the compensator was set with the central band on a cross hair (zero retardation), and its scale reading noted. The specimen was then stressed, by attaching to it a pan to which weights were added, and the compensator then adjusted to bring the central band on the cross hair, and the scale read.

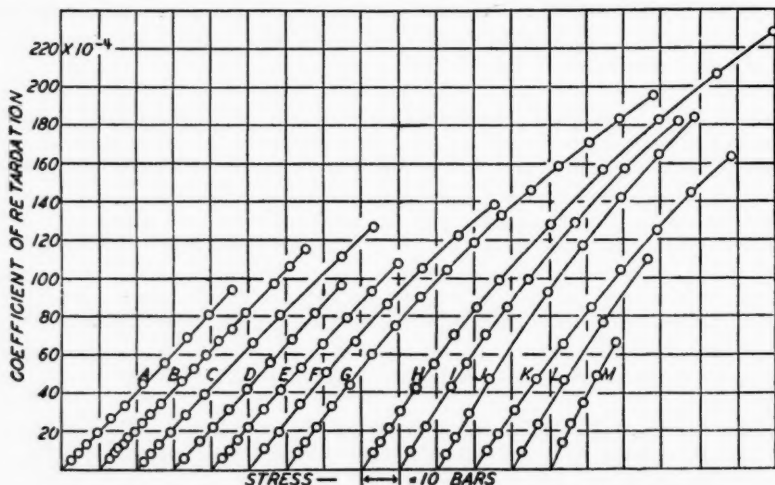


Figure 1—Relation of Coefficient of Relative Retardation to Tensile Stress

Compounds A to E represent rubber compounds made with organic accelerators, F to J, compounds of crude rubber and sulphur, K to M, compounds of purified rubber and sulfur. Each curve is plotted from a separate origin to avoid confusion. The stress relates to the actual cross section.

After the length between the reference marks on the specimen was read by means of the cathetometer, the compensator reading was again checked to ascertain whether optical creep had occurred. Successive additions of weight were made until optical creep was observed or until the sample broke, as happened with some of high sulfur content. The upper support which held the specimen was adjusted after each addition of weight to keep the constricted portion centered in the optical path. The pan was clamped before each addition of weight, and was released gently so as not to permit oscillation. No definite time schedule was followed in conducting the operations. The observations on a given specimen were usually made without interruption at 10 to 20 increasing stresses, and occupied about one to two hours. The temperature at which measurements were made was not controlled, but it was regularly observed and recorded.

4. Computation of Coefficient of Relative Retardation, Stress-Optical Coefficient, and Stress

The relative retardation per unit thickness is expressed by the relation,

$$\Delta n = \frac{R}{d},$$

where R is the observed relative retardation, and d is the thickness in the same units. When the relative retardation is measured by means of the compensator mentioned above, and the thickness is found from the thickness in the unstressed state and the elongation, this equation becomes,

$$\Delta n = \frac{(11,400 \Delta x)}{d_0} \sqrt{\frac{L}{L_0}}$$

where Δx is the change in setting of the compensator, 11,400, the compensator constant, L_0 and L , the original length and the length under stress, respectively, and d_0 , the original thickness.

The stress-optical coefficient is defined by the relation,

$$C = \frac{R}{Td} = \frac{\Delta n}{T}$$

where C is the coefficient, and T , the tensile stress. The stress-optical coefficient has the dimensions of the reciprocal of a stress. When the relative retardation is expressed in Ångstrom units, the stress in bars, and the thickness in millimeters, the stress-optical coefficient is given in brewsters.

The stress in bars was usually found from the relation,

$$T = 980.7 \times 10^{-6} \left(\frac{mL}{d_0 w_0 L_0} \right),$$

where T is the stress, m , the load in grams, and d_0 and w_0 , the thickness and the width, in cm., respectively, of the sample in the unstressed state. This stress relates, of course, to the actual cross section, not the original cross section which is commonly used in connection with stress-strain curves for rubber.

This equation for the stress, as well as the one for the coefficient of relative retardation involves the assumption that the reduction in thickness and the reduction in width of a stressed specimen are each proportional to the square root of the increase in length. In the case of one compound, designated as B in Table I, this assumption was verified by direct measurements with the screw micrometer gage on a number of specimens. These measurements gave an average value for Poisson's ratio as 0.502 at elongations up to 350 per cent. The amount by which this differs from 0.500 was less than the probable error of the determination.

Further evidence regarding Poisson's ratio may be adduced from measurements of the change of volume of rubber on stretching, provided the assumption is made that the ratio is the same in the thickness and in the width dimension. This latter assumption is reasonable in view of the well-known isotropic character of molded rubber of the "pure-gum" type.

Measurements of the volume change on stretching were made on compounds B, D, F, and G.⁸ None of these showed any appreciable change of volume at elongations up to 350 per cent. At an elongation of 400 per cent, compounds B and D decreased in volume by 1 or 2 parts per 1000; at 500 per cent, the decrease was 5 to 8 parts per 1000; and at 600 per cent, it was 10 to 15 parts per 1000. Compounds F and G, on the other hand, showed no significant change of volume at 500 per cent elongation, while at 600 per cent the volume decreased by 1 to 2 parts per 1000.

With the majority of the compounds the photoelastic measurements were terminated at elongations below 400 per cent. Neglect of the volume change on stretching probably occasioned no appreciable error in the case of these compounds, or in the case of compounds F and G which were measured at elongations up to 550 or 575 per cent. Compounds H and K were measured at elongations up to about

580 per cent, but in the absence of definite data on the volume relations for these compounds no definite estimate can be made of the probable error entailed by neglecting the change of volume on stretching at the higher elongations. It was, however, probably not great.

5. Relation of Coefficient of Relative Retardation and Stress-Optical Coefficient to Stress

When the retardation coefficients of the different rubber compounds were plotted against the stress, the relation was in some instances linear, while in other cases it showed a greater or less deviation from a linear function. It was found that the relations could be expressed by equations of the form,

$$\Delta n = aT + bT^2 + cT^3$$

where Δn is the retardation coefficient, T the stress, and a , b , and c are constants for any given rubber compound under specified conditions of measurement. For some compounds b and c are zero; the measurements on other compounds at stresses below about 65 bars are adequately represented by making c equal to zero, while at higher stresses c was not zero.

The coefficients, a , b , and c , of the above equation were determined for all the specimens investigated, and are here employed as a means of presenting the results of the investigation in concise form. The values of the parameters are given in Table II, along with other data regarding the determinations, including the tem-

TABLE II
SUMMARY OF PHOTOELASTIC MEASUREMENTS

Compound	Sam- ple Num- ber	Tem- pera- ture, °C.	Range of Elonga- tion, Per Cent	Range of Stress, ^a Bars	Parameters of Equation, ^b $\Delta n = aT + bT^2 + cT^3$			Difference between Values of Δn (Obs.) and Δn (Calc.) $\times 10^4$	
					$a \times 10^4$	$b \times 10^4$	$c \times 10^4$	Max.	Avg.
A	1	26.1	26 to 308	2.78 to 45.65	2.059	0	0	0.5	0.2
	2	27.7	26 to 324	2.77 to 51.1	2.044	0	0	0.4	0.2
	3	30.5	25 to 299	2.78 to 44.95	2.019	0	0	0.85	0.3
	1	24.0	26 to 323	2.73 to 55.0	2.092	0	0	0.4	0.1
	2	25.5	25 to 335	2.95 to 54.3	2.092	0	0	0.4	0.15
B	3	24.2	25 to 260	2.95 to 38.6	2.097	0	0	0.3	0.15
	4	22.4	13 to 261	1.68 to 40.0	2.108	0	0	0.7	0.2
	5	27.8	14 to 273	1.69 to 41.15	2.084	0	0	0.5	0.2
	6	24.0	25 to 258	2.96 to 39.5	2.091	0	0	0.6	0.2
	7	22.5	6 to 129	0.73 to 15.65	2.108	0	0	0.2	0.05
C	1	24.0	13 to 308	1.76 to 63.2	2.233	-0.00354	0	0.3	0.15
D	1	28.8	31 to 365	2.70 to 44.6	2.158	0	0	0.7	0.15
	2	24.4	33 to 348	2.82 to 40.45	2.155	0	0	0.8	0.25
E	1	...	30 to 365	2.72 to 49.4	2.267	-0.00175	0	0.3	0.15
	2	24.5	30 to 362	2.75 to 49.65	2.242	-0.00146	0	0.3	0.15
F	1	26.9	69 to 572	3.87 to 65.2	2.660	-0.00820	0	0.3	0.1
G	1	21.8	40 to 470	2.91 to 65.0	2.895	-0.01000	0	0.65	0.25
	1	21.8	40 to 556	2.91 to 96.95	2.895	-0.01127	0.000023	1.3	0.45
H	1	25.6	30 to 403	2.84 to 64.2	3.120	-0.01075	0	0.95	0.35
	1	25.6	30 to 506	2.84 to 109.5	3.120	-0.01258	0.000029	0.6	0.3
	2	31.7	34 to 582	3.29 to 163.6	2.988	-0.01170	0.000026	1.95	0.45
I	1	27.2	27 to 380	2.92 to 74.15	3.297	-0.01138	0	0.75	0.4
	2	27.3	27 to 383	2.95 to 74.6	3.275	-0.01110	0	0.8	0.3
J	1	27.9	19 to 345	2.20 to 68.5	3.509	-0.01216	0	0.75	0.35
K	1	26.0	58 to 581	3.41 to 68.4	3.005	-0.00909	0	0.7	0.3
L	1	25.3	32 to 296	2.83 to 35.95	3.531	-0.01313	0	0.25	0.1
M	1	25.0	31 to 142	3.57 to 17.3	4.108	-0.01466	0	0.25	0.1

^a Stress refers to actual cross section.

^b Δn is relative retardation per unit thickness, and T , stress.

perature at which the measurements were made, the range of stresses employed, and the corresponding elongations produced in the samples. The range of stress covered extended to between 50 and 100 bars in the case of most compounds, and to 164 bars in one instance. Values of the retardation coefficient ranged up to 100 to 200×10^{-4} in most instances.

Curves showing the relation of the coefficient of retardation to stress for a typical sample of each compound are presented in Fig. 1. The smooth curves were com-

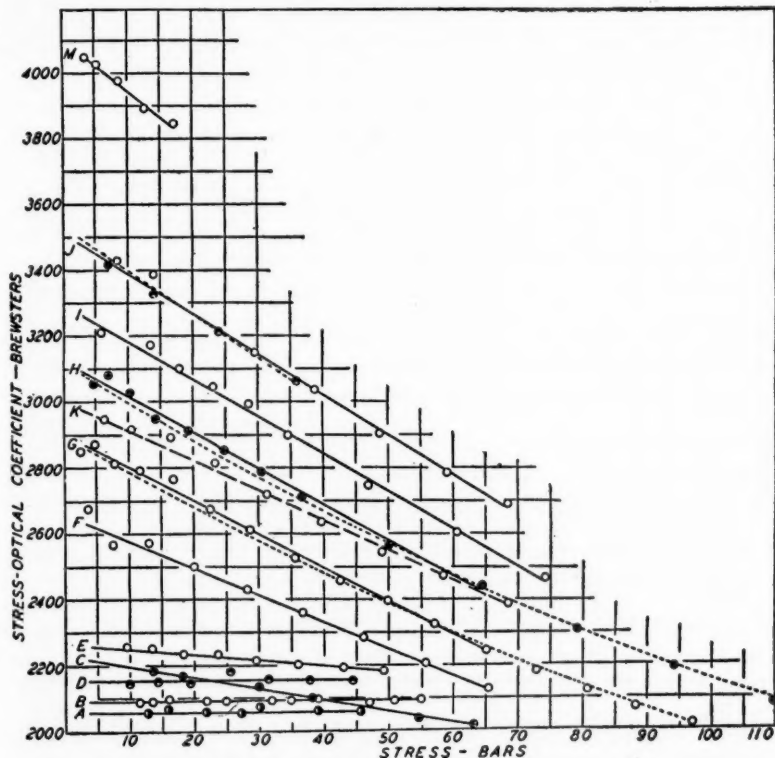


Figure 2—Relation of Stress-Optical Coefficient to Tensile Stress

Curves for compounds J and L almost coincide; the dotted curve refers to L. The solid curves for compounds G and H were computed from equations in a and b , the dotted curves from equations in a , b , and c . The stress relates to the actual cross section.

puted from equations using values of a , b , and c from Table II while the points shown represent observations. In most cases the points cannot be distinguished from the curves on the scale of the figure. The differences, however, were computed and are summarized in the last two columns of Table II. The average discrepancies range from 0.1 to 0.45×10^{-4} unit of the retardation coefficient for the different compounds, while the maximum discrepancies are from 0.25 to 2.0×10^{-4} . These relate to values of the retardation coefficient ranging up to 100 or 200×10^{-4} . The results obtained with specimens of compounds G and H are expressed by second-degree equations at stresses below 65 bars, and by third-degree equations for the complete range of observations which extend to about 100 bars. The second-de-

gree equations were found in order that the parameters a and b might be correlated with the composition, as is discussed in a subsequent part of this paper.

Measurements on specimens of compounds A and B were made at temperatures covering ranges of 4° or 5° . The results indicate a decrease in retardation coefficient of the order of 0.25 to 0.5 per cent per degree, but are not sufficiently precise to warrant the computation of temperature coefficients.

Stress-optical coefficients were found corresponding to all measurements of retardation coefficient. The coefficients for typical samples of the various compounds are shown in Fig. 2, plotted as functions of the stress. The smooth curves were found by means of the values for the parameters, a , b , and c , given in Table II while

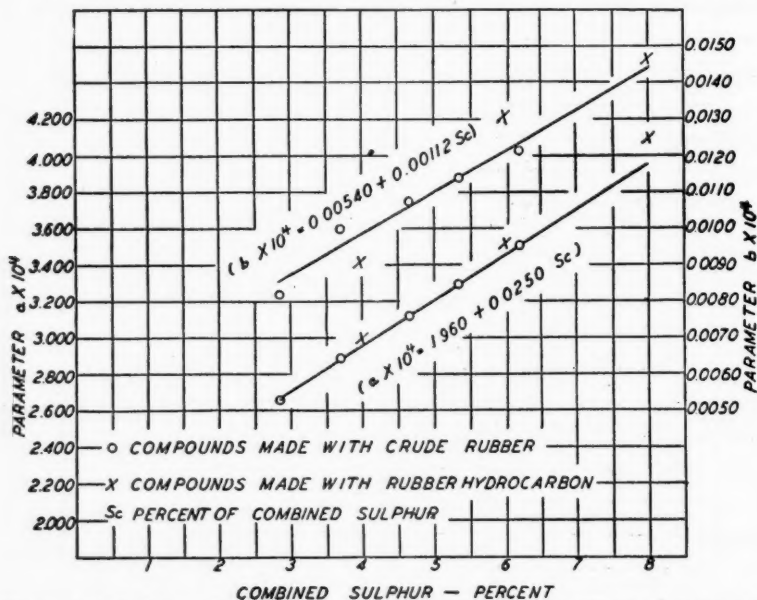


Figure 3—Relation of Parameters a and b to Percentage of Combined Sulfur in Rubber-Sulfur Compounds

The parameters are the coefficients in the equation, $\Delta n = aT + bT^2$, where Δn is the coefficient of relative retardation, and T the tensile stress. Values of b shown in the figure are negative in sign.

the points shown represent observations. In the case of compounds A, B, and D, the coefficient is constant and independent of stress. In the case of other compounds, the values for the coefficient decrease with increasing stress, the slopes and intercepts varying with the compound. For compounds G and H, straight lines, in terms of a and b represent fairly well the results at stresses below 65 bars; these are shown in the figure by solid curves. Measurements on these compounds at higher stresses, however, are well fitted only by equations in terms of a , b , and c , which are represented in the figure by the dotted curves.

At low stresses the values for the stress-optical coefficient show considerable scattering, for the reason that they represent the ratios of small values of the retardation coefficient and stress, and hence are not of high precision. In the figure the points at stresses below 10 bars have been omitted from some of the curves, to avoid confusion.

The numerical values of the stress-optical coefficient for the compounds made with

accelerators all fall between 2000 and 2300 brewsters. For rubber-sulfur compounds at low stresses, the values are from about 2600 to 4100 brewsters, but these decrease with increasing stress, and at relatively high stresses drop to as low as 2000 brewsters.

6. Relation of the Photoelastic Properties of Rubber to the Composition

The examination of the results presented in the previous section indicates that the rubber compounds fall into three groups as regards photoelastic properties. In one group are the compounds A, B, and D for which the parameters b and c are zero, the relation of coefficient of retardation to stress is linear, and the stress-optical coefficient is constant. A second group is made up of compounds from F to M, inclusive, for which the parameter c is either zero or has a small positive value while the parameter b has a relatively large negative value, indicating that the relation of the coefficient of retardation to the stress departs considerably from a straight line, and that the stress-optical coefficient decreases markedly with increasing stress. The third group is made up of compounds C and E, which fall between the two previous groups in respect to photoelastic properties.

This division into groups follows the mode of vulcanization. Compounds A, B, and D are vulcanized with the aid of organic accelerators, employing the minimum percentages of sulfur consistent with the development of good physical properties. Compounds F to M, inclusive, on the other hand, are rubber-sulfur compounds vulcanized without the aid of organic accelerators, while compounds C and E contain accelerators, but also contain more sulfur than the minimum required to develop good physical properties, and hence partake of the character of both the rubber-sulfur and the accelerated compounds.

When the measurements on the rubber-sulfur compounds are expressed in equations of the second degree, the parameters a and b both bear approximately linear relations to the combined sulfur content, as is indicated by the curves shown in Fig. 3. The points representing measurements on compounds containing rubber hydrocarbon are distinguished in the figure from those on compounds containing crude rubber; they might be represented by two slightly different curves, but this has not been done because data are available on only three compounds of the rubber hydrocarbon, and are not considered adequate to define an exact relation. One straight line was drawn through values of a for the compounds F to J, inclusive, and another straight line through the corresponding values of b . These lines represent with reasonable fidelity, the values of a and b for compounds K and L, but are somewhat too low in the case of compound M.

The equations for the relations of a and b to the percentage of combined sulfur are shown on the figure. These lead to the following expression for the coefficient of relative retardation of rubber sulfur compounds,

$$\Delta n \times 10^4 = (1.960 + 0.0250S_c)T - (0.00540 + 0.00112S_c)T^2$$

where S_c is the percentage of combined sulfur and T is the tensile stress. This relation is applicable to compounds containing 2.85 to 6.2 per cent of combined sulfur, and to measurements at stresses up to 65 bars.

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The Structure of Rubber and the Mechanism of Elastic Stretching

Edward Mack, Jr.

CHEMICAL LABORATORIES, OHIO STATE UNIVERSITY, COLUMBUS, OHIO

Rubber seems to be unique in the magnitude of its elastic extensibility. No adequate explanation of its behavior has ever been given.

The supposition that mere high molecular weight alone can account for pronounced elastic properties is not permissible. High molecular weight may be *necessary* but it is not a *sufficient* condition. In any elastic-stretch effect, at all comparable in magnitude with that of rubber, we must necessarily expect to find *two* features present, whatever the particular mechanisms may be by means of which these two features are achieved, namely: (I) there must be some mechanism whereby the molecules involved can change their width and depth dimensions into length, upon the application of a stretching force; and (II) there must be some mechanism for automatic retraction.

The closest approach to a satisfactory picture is perhaps Kirchhof's assumption of a spiral¹ molecule, later developed by Fikentscher and Mark,² Hauser,³ and others. Although this explanation may have provided satisfactorily for (I), it has been weak and defective in the more essential particular, since it has failed to indicate any operable mechanism for automatic retraction.

In the first place, when we examine into the potentialities of the rubber molecule in a search for centers of attractive force sufficiently cogent to implement a mechanism for compulsory folding, we are practically limited to a consideration of two possibilities: either (a) that the residual valences of the double bonds (the effective force assumed by Fikentscher and Mark), or (b) that the van der Waals attractive forces between hydrogen atoms (on the surfaces of the molecules) act in this capacity. Possibility (a) may be eliminated as being extremely improbable in itself, and far less probable than (b), on the following grounds. (1) When the rubber molecule is extended, the double bonds are spaced much too far apart to permit the van der Waals forces (or any other forces such as residual chemical forces) between neighbor double bonds to become operative. Such forces fall off extremely rapidly with increasing distance between centers of attraction; and it is not easy to see how the double bond valences theory can surmount this serious difficulty. (2) If the residual valences of the double bonds are in fact such powerful centers of attraction one would expect the boiling point of liquid ethylene, $\text{H}_2\text{C}=\text{CH}_2$, to be much higher than that of liquid ethane, $\text{H}_3\text{C}-\text{CH}_3$. But on the contrary, the boiling point of ethylene is lower, only about 169.4°A. , whereas that of ethane is about 184.9°A. Thus it seems clear that two hydrogen atoms (attached to adjacent carbon atoms within a molecule) attract neighbor hydrogen atoms more strongly than the residual valences of a double bond attract neighbor double bonds and neighbor hydrogen atoms. (3) Staudinger⁴ and Leupold, who claim to have shown that practically completely hydrogenated rubber still possesses to a considerable extent the elastic properties of natural rubber, attempt to score the point that the double bonds, therefore, cannot be an essential part of the retractive mechanism. The validity of this criticism, of course, depends on the reliability of their own conclusions. No quantitative data have as yet been pre-

sented either as to the degree of hydrogenation of their product or as to the degree of its elastic extensibility.

We know that the van der Waals forces of attraction between hydrogen atoms (attached to carbon atoms), thus $\text{—C—H}::\text{H—C—}$, are quite large, as is made evident by the magnitude of heats of fusion and heats of vaporization of *normal* hydrocarbon chain molecules, for example. Figure 1a, shows a model of *n*-hexane. The carbon atoms (radius 0.77 A. U.) are attached together at tetrahedral angles, and form the backbone of the molecule. The hydrogen atoms (of equilibrium domain radius 1.29 A. U.)⁵ are attached to the carbon atoms (C—H internuclear distance 1.08 A. U.) at tetrahedral angles also, and they form an outer skin or sheath which envelops the carbon chain completely. Behind every hydrogen atom in the drawing (except the end hydrogens) there lies another hydrogen atom, to form the pair of hydrogens on each carbon, CH_2 . When such a molecule escapes by evaporation from a liquid surface, as in Fig. 1b, the van der Waals contacts must be broken, on the average, at about 15 hydrogen atoms, although possibly about 20, where the bottom surface of the molecule, one side surface, and one end, contact with neighbor molecules lying in the surface of the liquid. It makes no difference whether the surface molecules are lying flat or standing vertically in the surface. Since the molar heat of vaporization of *n*-hexane at 0° is 7675 cal.,⁶ the energy required to drag 1 gram-atom of hydrogen (bonded to carbon, C—H) off a hydrocarbon surface would be about 500 cal. at room temperature ($7675 \div 15 = 512$). This value will be used later to calculate the work of stretching rubber.

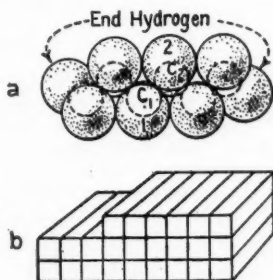
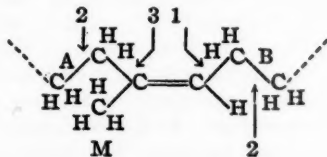


Figure 1

In the second place, if we examine the rubber molecule for a possible mechanism for extensibility, it would seem that we are limited entirely to rotation on C—C bonds (and to the extremely small molecule extension due to slight bending of bonds). In the accompanying structural formula of a section of the *extended* rubber [molecule chain, the C—C bonds are numbered 1, 2, 3 to correspond with the scheme used in the model of Fikentscher and Mark. Rotations about

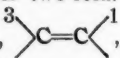


bonds 1 and 3 are easy and free. The angles through which the two respective rotations occur, namely, the rotation of C_2H_4 group A on bond 3 and of C_2H_4 group B on bond 1, are determined by structural features within the formula

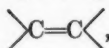
section, to be explained presently. Rotation on bond 2, with in the C—C groups, cannot occur, or perhaps, more correctly, it does not occur. It is not so much the steric hindrance of the large-sized hydrogen atoms that prevents this rotation, but rather the strong van der Waals forces of attraction between the hydrogen

atoms on the two neighbor groups. In Fig. 1a, hydrogen atom 1 and the hydrogen atom directly behind it, both attached to carbon atom C_1 , are tightly locked to hydrogen atom 2 and the hydrogen atom directly behind it, both of which are attached to carbon atom C_2 . It requires a strong impulse to cause rotation over these potential humps, unless, of course, a better hydrogen-to-hydrogen contact could be established by rotation. It is not apparent how any such betterment could be achieved by rotation on bond 2 of the C_2H_4 groups in the rubber molecule, and it is extremely probable that these groups act as fairly rigid blocs.

Function of the Double Bond.—The function of the double bond is two-fold.

- (1) It provides enough free space about the doubly bonded carbon atoms, , to permit free rotation on bonds 3 and 1. (2) It functions in such a way as to throw the C_2H_4 groups either into the *cis* or *trans* positions. The unique elastic properties of natural rubber develop only when the C_2H_4 groups are *cis*.

Mechanism of Elastic Stretch

The details of this mechanism may be explained by reference to approximately scale drawings of the molecule models. In Fig. 2I, is given what we may call a side view. The double-bonded carbon atoms, , are shown at the middle,

with the single bonds radiating at 120° angles, all in the plane of the paper. Attached to one of these bonds is the single hydrogen atom H_m ; attached to another (lower left) is the methyl group, carrying three hydrogen atoms (directly behind H_m lies another hydrogen which we shall designate as H'_m). All of the hydrogen atoms, except H_m , are attached to their respective carbon atoms at tetrahedral angles. The various atoms occupy the positions shown, in I, when the rubber molecule is *extended*.

The methyl group is free to rotate, but it orients itself as indicated because one of its hydrogen atoms will then contact with H_m , whereas if it turns so as to present two hydrogen atoms to H_m , no contacting occurs. Thus the two hydrogen atoms, H_m and H'_m , place themselves just beneath C_2H_4 group A, and contact, respectively, with hydrogen atoms a_1 and a'_1 (which is behind a_1) of group A. A top view, looking down on the eight hydrogen atoms of groups A and B is given in II.

Now, when the retraction mechanism operates, two things happen. First, Group A rotates through approximately 40° . Let us set up a reference point on the paper (in II), marked Y. Then the part of the C_2H_4 group A indicated by X turns around (on bond 3) so that X is brought close to Y, as shown in III. The reason for the rotation is the achievement of a larger number of hydrogen-to-hydrogen contacts after the rotation. In the extended configuration, in II, there are *four* hydrogen contacts made by group A, namely, a_2 with b_2 , a'_2 with b'_2 , a_1 with H_m , and a'_1 with H'_m . But after the rotation, in III, group A makes *six* hydrogen contacts, namely, a'_2 contacts with both b_2 and b'_2 , a_2 contacts with H_m , a_1 contacts with both H_m and H'_m , and a'_1 contacts with H'_m . Therefore position III has the advantage over position II in affording *two more* hydrogen contacts. The impelling force which causes the rotation is the van der Waals attraction between hydrogen atoms; and the plausibility of our appeal to these forces is very great because they are required to operate over only extremely small distances, less than 1 A. U.

Secondly, after group A has turned, group B then executes a rotation through about 100° (from W to Z in III), to give the final completely retracted form shown

in IV. In the configuration of III, group B makes *four* hydrogen-to-hydrogen contacts, both b_2 and b'_2 with a'_2 , and both b_1 and b'_1 with H_a (beneath). In IV, group B makes *five* hydrogen osculations, namely, b_1 and b_2 both contact H_a , b'_1 contacts a'_1 , b'_1 contacts a'_2 and b'_2 contact a'_2 . Configuration IV represents an improvement of *one* contact over III. The van der Waals forces of attraction of both a'_1 and a'_2 (in III) for b'_1 are required to function over a considerable distance, about 3 A. U. But it is extremely likely that the oscillation of group B about bond 1, due to thermal agitation, would bring b'_1 well within range of these forces. If group A rotated initially clockwise, as in III, then group B would rotate counter-clockwise; but if group A rotated toward Y' then group B would rotate clockwise to contact with it.

Thus, the retracted form IV possesses altogether *three* more hydrogen-to-hydrogen contacts internally, within the configuration, than the extended form II. By

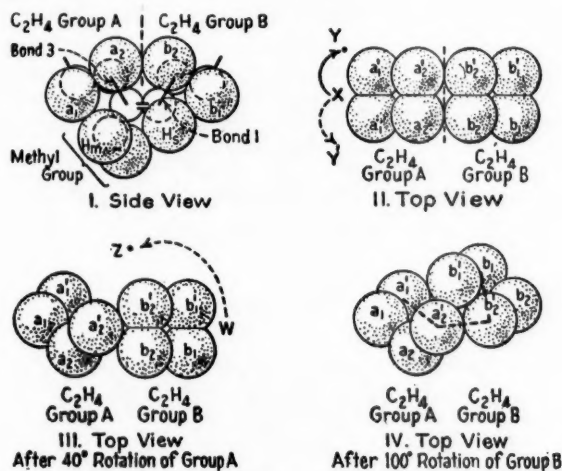


Figure 2

pulling out the retracted and folded form we do work against the van der Waals forces of attraction, residing in the extra hydrogen contacts, and store potential energy (of bond rotation). Upon release of the stretching force, rotation automatically occurs to the retracted form, a condition of smaller potential energy. In somewhat different words, and by analogy with the evaporation of hydrocarbon molecules from a liquid surface, we may say that in the stretching process three atoms of hydrogen are dragged off a virtually liquid surface, and in retraction three atoms of hydrogen spontaneously condense, for that portion of the rubber molecule shown in Fig. 2. If we wish to coin a name for the mechanism by which the rubber molecule extends and retracts we might, therefore, appropriately call it a "hydrogen-evaporation-condensation" process. The mechanism resembles evaporation \rightleftharpoons condensation rather than melting \rightleftharpoons crystallization because when a hydrocarbon molecule escapes by evaporation from a hydrocarbon surface, all of the hydrogen-to-hydrogen contacts that are broken, are broken completely, as is also true of the present rubber stretch mechanism; whereas when such a molecule leaves a crystal lattice and passes into a melt, the number of hydrogen-to-hydrogen contacts may be somewhat diminished, but the significant change is

that the extra load of kinetic energy which the molecule has acquired prevents it from being retained rigidly in the lattice.

Since group A, in Fig. 2, functions as a group B for the next pair of doubly bonded carbon atoms in the rubber chain, lying to the left, and since group B functions as a group A to the right, there will be an improvement of three hydrogen contacts, in passing from the extended to retracted form, for every double bond throughout the length of the whole rubber molecule. Since we already know approximately the energy required to evaporate a gram-atom of hydrocarbon-hydrogen, we have available the basis for a calculation of the work required to stretch rubber, if we can estimate the number of double bonds, or of C_5H_8 groups in unit volume of rubber. Before we proceed to this calculation, however, it would be well to discuss the gutta molecule, as well as the shape of the rubber molecule and the problem of degree of elongation.

The Gutta or Balata Molecule.—The important difference between the rubber and gutta molecules may be illustrated in Fig. 3. Both molecules are shown *ex-*

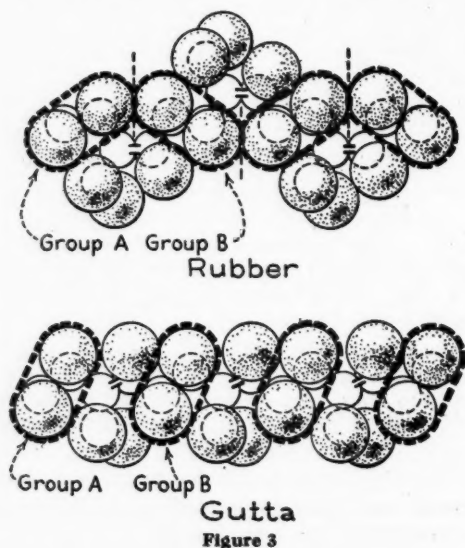


Figure 3

tended. In rubber, it is the fact that the A and B groups are in the *cis* position, and are consequently tilted *toward* one another, that allows group B, rotating through about 100° , to make an improved hydrogen-to-hydrogen contact with group A (which has itself rotated through about 40°). In gutta the A and B groups are *trans*. Group B is not tilted toward A, but lies parallel to it, and no amount of turning of B will bring it any nearer to A. Nor does rotation of any sort improve the hydrogen contacting of group B in any manner. It already makes four hydrogen contacts, two with the hydrogen atom of the methyl group, and two with the single hydrogen atom *trans* with respect to the methyl group. It unquestionably retains this fixed position permanently (with respect to the hydrogen atom and methyl group lying to its left).

However, group A in the gutta molecule does rotate through 40° , as in the case of rubber; although it is to be noted that there is a gain of only *one* hydrogen contact in this rotation, as compared with *two* in rubber. For, while the lower

end of group A in the gutta molecule, Fig. 3, gains two contacts with the methyl group in executing the 40° rotation, it loses one contact with the single hydrogen atom (*trans* with respect to the methyl). It is to be kept in mind that every one of the C_2H_5 groups in gutta acts as an A group to the right and as a B group to the left, with the result that the C_2H_5 are rigid blocs, turning through 40° on bond 3 (see Fig. 2).

Thus the total retractive effect in gutta would be only one-third as large as in rubber, per C_2H_5 group, and in gutta the extensibility would be quite small because the rotation through only 40° would not affect the length appreciably. The 50:50 chance of 40° rotation of the C_2H_5 group either clockwise or counter-clockwise would thus probably lead to a zig-zag molecule with a long axis which is straight for the most part, but occasionally bent into long arcs, or into gross zig-zags. A tangled mass of such molecules, all of them possessing slight extensibility, could well exhibit the slightly elastic behavior characteristic of gutta.

Shape of the Rubber Molecule and the Problem of Elongation.—It is extremely difficult to demonstrate the shape possibilities of the rubber molecule chain without the aid of 3-dimensional scale models. But a rough idea of the possibilities may be conveyed diagrammatically. In Fig. 2IV, the directions in which the three 2-carbon sections, C—C, C=C, and C—C, lie as viewed from above, after the 40° and 100° rotations have occurred, are indicated by the heavy dotted lines.

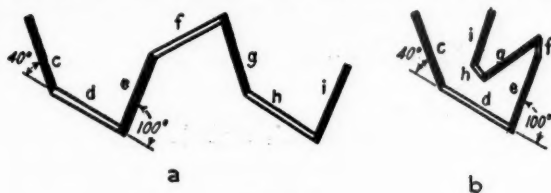


Figure 4

Remembering that the 40° rotation may occur in either direction, let us consider Fig. 4, where the C=C section is represented thus \equiv . At (a) a zig-zag shape is shown, obtained by allowing the 40° rotations to occur alternately along the chain, first in one direction and then in the other. Such a retracted shape pulls out to almost twice its initial length. In (b) the 40° rotation on $\equiv f$ is in the same direction as on $\equiv d$; on $\equiv h$ it is opposite. $\equiv f$ is directed up out of the plane of the paper (in b). The section g lies above e, and i lies above g. This shape has an elongation of about 4.

Obviously with about 1000 C_2H_5 groups per molecule (molecular weight about 68,000) and with the potentiality of either clockwise or counter-clockwise 40° rotation for every C_2H_5 group, there will be an enormous number of possible shapes, in fact 2^{1000} , except in so far as the crowding by neighbor molecule strands prevents the formation of otherwise possible shapes. True spirals would probably not be produced, at least not if the 40° and 100° rotations are compulsory. But if the 100° rotation is frequently prevented from attaining its full value by the interference of vicinal groups on neighbor molecules, so that the rotation takes place through only 50° to 75° (on condition that a betterment of hydrogen contact is obtained with the neighbor groups), tight or loose spirals of various degrees of pitch might be formed. This is not very likely; one would rather expect to find folded zig-zags and "S"-shaped forms of various sorts.

Nor does x-ray examination of retracted rubber give us any help at all at present in connection with molecule shape. The x-ray diffraction pattern of retracted

rubber resembles the typical liquid or amorphous pattern. All we could hope to get out of it would be that, already knowing the structure of the C_5H_8 link, we could attempt to justify this structure from the x-ray data; that is, we could treat the retracted rubber as a liquid made up of C_5H_8 groups. In the completely or largely extended form of the molecule, the x-ray interferences from the regularly spaced C_5H_8 groups along the whole length of the straightened molecule lying in the direction of stretch would produce a typical uni-axial x-ray pattern, as indeed it does. But we know this much already for extended rubber, at least by deduction from the geometrical considerations here presented. The x-ray work has, of course, emphasized the point that the arrangement of the parts of the molecule is random in retracted rubber, and anisotropic in extended rubber. However, there would seem to be no justification for an interpretation of the diffraction pattern of retracted rubber as indication of the presence of spirals. This may be the true solution, but it is ambiguous; there may be many other solutions which fit the x-ray data equally well.

It is not easy to predict what the elongation of the average molecule would be. But in view of the probability that close-packed chain sections would be favored because of the severe space restrictions imposed by neighbors, it would not be unfair to assure an average elongation of about 3. The degree of elongation pos-

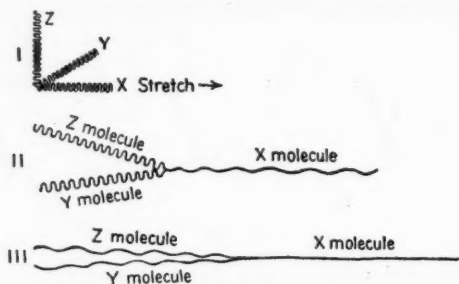


Figure 5

sible with any particular molecule depends not only on its shape, but also on its original position, occupied in the matrix of the rubber with respect to the direction in which the piece of rubber is eventually stretched (to consider only uni-directional stretching). From the well-known fact that a piece of rubber is isotropic with respect to stretch, unless it has been milled or racked or been given violent mechanical uni-directional treatment of some sort, it follows that the general orientation of any chosen molecular axis, such as the long axis, must be perfectly random and haphazard. In other words, we not only have a practically infinite number of possible molecule shapes, but we also have them tangled together in a practically infinite number of different directions. It is possible to obtain an approximate analysis of the situation, nevertheless, in the following manner.

Let us suppose that in a small cubical volume of rubber we have three molecules of average shape, and each of potential elongation equal to 3, arranged along three rectangular coordinates, x , y , and z , as shown in Fig. 5I. The direction x is parallel to the direction in which stretching is to occur, y is perpendicular to the plane of the paper. All of the other molecules, lying in an enormous number of different directions in the solid angle subtended by x , y , and z axes, will exhibit an average elongation behavior which will be approximately the same as the combined effect produced by stretching these three molecules. The initial length of this small cube of rubber is the length of the x -molecule, and we may set it equal to 1.

Upon the application of the stretching force, the x-molecule will unwind first since, because of its more favorable orientation, it is more susceptible to the unwinding leverage at its rotatable link joints. In II of Fig. 5, the x-molecule is shown practically completely straightened out to almost three times its initial length. During this earlier portion of the stretch, as the length of the rubber piece increases, and its cross section diminishes, the axes of the y- and z-molecules will ride around with the mass of rubber, and will line up more and more in the direction of stretching (if slippage is prevented). As they do so these molecules will themselves begin to unwind, and will eventually be straightened out almost completely in the line of stretch, as shown in III. In this way the original length of 1 will become extended to a final length of about 6. It should be pointed out that the length of the z-molecule will *not* be added to the length of the y-molecule, to give a total elongation of about 9. For, as the cross section diminishes, as width and depth both transform themselves into length, the z-molecule will be performing the same function in the width dimension which the y-molecule is simultaneously performing in the depth dimension; and the two molecules will, finally, at the end of the stretching, be lined up as two practically parallel strands side by side.

At any rate it would seem to follow logically on these geometrical grounds that the elongation of a macroscopic piece of rubber will be very nearly *twice* the elongation of its average molecule, oriented with its long axis in the direction in which the stretching force is applied. Furthermore, this conclusion is valid no matter in what direction one chooses to stretch the piece of rubber, since the rectangular and mutually perpendicular reference axes, x, y, and z, may be shifted to any desired position to accommodate the direction of stretch, because of the isotropic character of the rubber. It would not be quite fair to claim that an elongation substantially in agreement with the observed elongation has thus been predicted. The average molecular elongation of about 3 was only a rough guess. (It might well be 4 or 5.) We may say, however, that there is clearly a sufficient and probable range of rubber molecule shapes, and of rubber molecule elongations, to provide the basis for an explanation of how rubber can be made to stretch as much as it is observed to stretch.

The Work of Stretching Rubber

During the first stages of the stretching process it has been observed that a much smaller force is required to produce a given extension of rubber than during the later stages, that is, if applied stretching force is plotted against elongation (as in Fig. 7), the curve rises more and more steeply toward the end of the stretch. The explanation of this stress-strain curve would seem to be as follows.

It is to be kept in mind that the retractive force at any stage of stretching depends on the population of bond rotation mechanisms that have been unwound at that stage, since van der Waals forces at all of these are tugging to achieve retraction. In Fig. 5, the unwinding of the x-molecules would in itself give an extension from an initial length of 1 up to about 3, and this would be still further increased by the mere partial riding around of the y-molecules and the z-molecules to give a total extension of about 4, without having unwound more than about one-third of the number of the 100° rotation mechanisms (B groups), which would of course unwind before the A groups (40°), because only one hydrogen contact is involved. Thus, only about one-ninth of the total hydrogen contacts would have been broken at this stage. The plot of this first portion of the stretch is given by the line x (100°), in Fig. 6.

Upon still further stretching, the y- and z-molecules unwind, and result in an extension in length up to a total of perhaps 5.5. But to unwind them a much larger stretching force must be applied because these two kinds of molecules provide twice as many hydrogen contacts (100° rotation) as the x-molecules. Furthermore, if twice the stretching force is applied, the unwinding leverage would take hold on the A groups (40°) of the x-molecules, so that by the time the length had increased to 5.5 times the initial length, five-ninths of the total hydrogen contacts would have been broken. The plot of this stage is indicated by the line x (40°); y, z (100°).

Then the A groups of the y- and z-molecules unwind, bringing the length up to perhaps 5.9, with the breaking of the remaining four-ninths of the hydrogen contacts, indicated by the line y, z (40°). Superimposed on this last increment in the stretching force, and perhaps to some extent on some of the earlier increments, just before the breaking load is reached, would be a considerable force required to do work of lateral compression, of pushing molecules together sideways into awkward positions, of forcing contacting atoms of neighbor molecules together until repulsive forces develop, and perhaps also of bond bending.

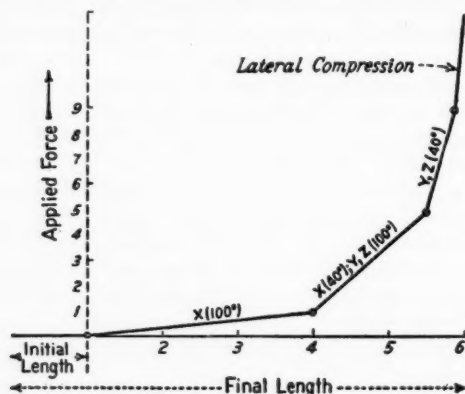


Figure 6

The foregoing analysis is very rough. For example, the line x (100°) would really rise more steeply, since many molecules oriented out of the line of stretch would almost immediately become subject to the unwinding leverage. However, the general shape features of the stress-strain curve emerge from these geometrical considerations.

The observed work of stretching rubber can be accounted for as follows. The over-all dimensions of the C_6H_8 group are about $6 \times 5 \times 4.4$ A. U., giving a volume of about 132×10^{-24} cc. On the supposition that a 1 cm.³ of rubber is made up of such closely packed groups, there would be 7.6×10^{21} C_6H_8 groups present (i. e., $1 - 132 \times 10^{-24} = 7.6 \times 10^{21}$). This is 0.0125 gram-molecule of C_6H_8 (i. e., $7.6 \times 10^{21} \div 6.06 \times 10^{23} = 0.0125$). This would yield a density for rubber a little greater than 0.85 (i. e., $0.0125 \times 68.06 = 0.851$), as compared with a density for natural rubber of about 0.9. Actually, of course, in natural rubber a certain amount of useless material is present, partially polymerized or partially broken-down molecules and the mingling of this material of relatively low molecular weight into the crevices and interstices of the rubber matrix could readily produce a slightly enhanced density.

Since three hydrogen-to-hydrogen contacts are broken in every C_5H_8 group, there would be 0.0375 gram-atom of hydrogen "evaporated" upon complete stretching of 1 cm.³ of natural rubber. As calculated previously, about 500 cal. are required to drag one gram-atom of hydrogen (C—H) off a hydrocarbon surface. Consequently, the predicted work of stretching 1 cm.³ of rubber is about 18.75 cal. or, in mechanical units, about 800 kg.-cm. This compares favorably with the 275–550 kg.-cm. actually observed for natural rubber and vulcanized rubber as shown, for example, in Fig. 7. It is to be remembered that the predicted value was for almost "perfect" rubber; there may well be not as many as 7.6×10^{21} C_5H_8 groups in 1 cm.³ Furthermore, not quite all of the A groups on y- and z-molecules may be unwound when break occurs; the value of 500 cal. may be a little too large; and the fraction of the total work attributable to lateral compression (indicated by the unshaded area in Fig. 7) is uncertain. The total work of stretching is to be portioned out to the various stages, as energy areas, in accordance with the shape of the stress-strain curve.

Two other matters now deserve consideration.

(1) In the Fikentscher and Mark model² theory, where the implementing force for retraction was assumed by its authors to be the residual valences of the double bonds, the retractive mechanism should obviously be destroyed by even an only fairly complete saturation of the double bonds with hydrogen. In terms of the present theory, however, we would expect substantial elastic properties if, after hydrogenation, a residue of a few double bonds per molecule is left. The point may be clarified with the aid of Fig. 8. After hydrogenation the molecule would lie in straight line sections like regular *normal* hydrocarbon chains (like Fig. 1) except for the side-chain CH_3 groups and except for the few double bond van der



Figure 8

Waals mechanism "joints" scattered randomly along the length of the molecule. In these straight sections of the chain, as we have represented them in the drawing, there would be perhaps 100–150 of the original C_5H_8 groups. The molecule would have a vastly smaller range of possible shapes than the original rubber molecule, but it could coil into spirals or zig-zags, or S-shapes. The extensibility of a tangled matrix of such molecules, randomly shaped and randomly oriented, would approach that of rubber; indeed the elongation could well be as large as in rubber, were it not for the probably more severe restrictions imposed by lateral compression. The behavior along the x, y, and z directions would be the same as that already described.

The strength of such a hydro-rubber would be very small as far as the unwinding of the small population of groups A and B is concerned. For this reason the first portion of the stress-strain curve would be very flat. But because of the development of lateral compression relatively early in the elongation, the curve would soon rise sharply to appreciably large values of applied stretching force.

Whether or not this prediction of some considerable elastic properties for hydrogenated rubber is substantiated by the facts depends on whether or not Staudinger's more recent conclusions are corroborated.

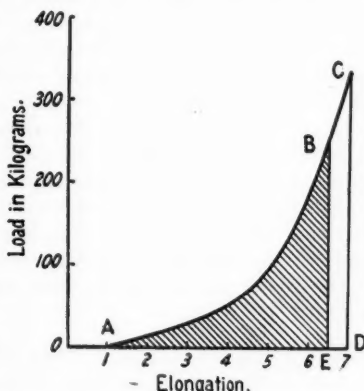


Figure 7

(2) It is to be expected that a slight improvement in the hydrogen contacting, around the external surfaces of the C_6H_5 groups, would come about during the later stages of stretching, since it would then be easier for the straightened anisotropic molecule strands to contact more perfectly with neighbors than in the random arrangement of the retracted condition. It might therefore be supposed that such an improvement in hydrogen-to-hydrogen contacting would prevent retraction. It is very doubtful whether the gain in the number of intermolecular contacts is anywhere nearly as large as the loss in intramolecular contacts resulting from the unwinding of the A and B groups, and furthermore it seems likely that the improvement in hydrogen contacting laterally between molecules at certain points is largely offset by the development of restoring repulsive forces due to lateral compressions at other points. It is difficult to evaluate the factors of the situation. It is possible, but doubtful, that this improved hydrogen contacting may operate to diminish the work of stretching rubber, and thus be one of the factors in causing the discrepancy between the predicted and the observed work of stretching.

Heat Effects in Rubber

It is well known that rubber, stretched and still loaded, will retract appreciably and lift the load, when the rubber is warmed. This is to be expected. The addition of heat would amplify the oscillation about the rotatable joints scattered along the length of the extended rubber molecules, particularly so in the extended state where van der Waals forces are tugging strongly to effect retraction. The time-averaged length of the molecules would of course become shorter, and partial retraction would occur. It is to be remembered also that near complete extension the more or less parallel molecule strands are pushed together tightly in lateral compression, and any increase in thermal agitation would produce a forced lateral expansion and a longitudinal contraction.

Retracted rubber, on the other hand, would *expand* (isotropically) when warmed, because of amplified oscillation at the turning bonds, but not very readily because of the resistance offered by the *folded* van der Waals mechanism "joints." If heated sufficiently, however, the time-averaged positions of the joints would be almost completely *unwound*, and the rubber would lose its elastic properties and assume the characteristics of a viscous "tacky" liquid. If the heating be not carried too far, the rubber would regain essentially its initial properties upon cooling; but, if unduly heated, thermal decomposition would disorganize the matrix and leave it permanently "sticky."

If largely extended rubber is chilled sufficiently it will not retract when the stretching load is removed; although, if it is allowed to warm up again, it will, at a characteristic temperature, jump suddenly back into retracted form. The extended molecule strands, lying together side by side, and pushed together by severe lateral compression, undoubtedly become locked in position at certain points by the fitting together of protruding atoms and groups into notches and reentrant angles, since even the completely extended molecule presents a surface contour which is zig-zag (see Fig. 3). Upon release of the stretching load, before normal retraction can then set in at room temperature, the tense molecules are dependent upon thermal agitation to disengage these mechanical obstructions to longitudinal motion. It is thus readily apparent how a fairly small drop in temperature could "freeze-in" the surfaces of the molecules and cut the thermal agitation sufficiently so that it would not be large enough to unlock the neighbor molecule strands.

The so-called *Joule* effect deserves consideration. Natural rubber and chloroprene rubber (but not other synthetic rubbers) upon extension become *warm* and,

upon retraction either with or without load, become cool. Bock and Bostroem⁷ very ingeniously calculated the heat effect for different degrees of elongation from their calorimeter measurements of the heat of swelling of rubber in benzene. They examined finely divided unstretched rubber, and rubber stretched to various degrees and stabilized by cooling to 8° (and also finely divided), and found a liberation of heat roughly proportional to the amount of elongation. For example at 658 and 821% elongation, the heats evolved were 5.24 and 6.80 calories per gram of rubber.

The evolution of heat is probably due to two effects: first, the improved intermolecular hydrogen contacting, following stretching. Since these contacts do not have to perform much external work in establishing themselves, but are brought about by a mechanically driven crowding together and alignment of molecules, heat would be evolved. The effect is akin to the Joule-Thomson effect in a hydrocarbon vapor. Since, however, the improvement in hydrogen contacting between neighbor molecules is probably really very slight, as we have already previously suggested, it is to be doubted whether this is an important factor in the Joule effect.

Second, and more significantly, the evolution of the heat is closely analogous to the evolution of a heat of crystallization, particularly of a liquid which is forced to crystallize above its normal freezing point by application of pressure. The freezing point of isoprene, C_5H_8 , is -120° . By the application of sufficient pressure we can raise its freezing point practically as much as we wish. This results because the applied pressure restricts the amplitude of the thermal motions of the molecules by squeezing the molecules together. If, with suitably delicate manipulating tools, we could grasp the two ends of a liquid isoprene molecule and hold it fixed, it would "freeze" far more easily than when possessed of its full quota of thermal agitation. In effect, this is really what happens to the C_5H_8 groups, polymerized to form a rubber molecule chain. They are fastened at both their ends, and the thermal motion of a C_5H_8 group is practically restricted to rotation about bonds. Consequently the individual groups freeze more easily than free isoprene molecules, although the groups are still "liquid" in retracted rubber at room temperature.

If, however, we still further restrict the thermal motions, and indeed practically remove the possibility of rotation on the bonds by stretching the molecules taut, and if in addition we squeeze the molecules together tightly in lateral compression, we may raise the freezing point sufficiently to cause crystallization at room temperature, whereupon the heat of crystallization is evolved. Upon release of the restraints, melting occurs and the heat of fusion is absorbed.

Further, it is likely that only the C_2H_4 groups B freeze. The A groups unwind with difficulty and most of them are unwound only near the end of the stretch. Even then the tendency of the A groups to rotate into retracted form is not much more than just balanced by the stretching load, and they are therefore ideally conditioned for appreciable amplitude of rotational oscillation, and are by no means held tautly stretched. The molar heat of fusion per CH_2 group is about 1000 cal.⁸ Therefore, for a mole of B group it would be about 2000 calories, and for the number of moles of B group in 1 g. of rubber (or 1 g. of C_5H_8) it would be about 29 cal. ($2000 \div 68 = 29$). This is to be compared with 6.8 cal. actually found by Bock and Bostroem, above. The meaning of this ratio of predicted to observed heat effect, 29:6.8, probably is that only about one-fourth, or one-third, of the B groups crystallize, namely, those on the x-molecules, initially oriented near the line of stretch. These are the only ones eventually pulled taut enough to freeze. These groups straighten out first, and thereafter are subjected

to the full force of the increasing stretching load which gradually tautens them more and more effectually, while the other B groups on y - and z -molecules are still being unwound, and never sufficiently tautened to freeze.

Accordingly, we would expect the Joule effect to increase at lower temperatures, since more of the groups would be able to freeze, and to decrease at higher temperatures. It is probably the junk materials, more or less oily sirupy hydrocarbon materials of relatively low molecular weight, that are responsible for preventing the development of the Joule effect in the synthetic rubbers (except in chloroprene). Such foreign molecules *lower* the freezing point, by interfering with the complete unwinding of the rubber molecules. For the same reason they prevent the development of the anisotropic x-ray pattern.

Attention should be directed to another interesting effect. If stretched rubber is allowed to retract without load, the van der Waals forces at the rotation joints would do very little work, merely that of retracting the unloaded rubber. Hence considerable heat should be liberated, an appreciable fraction of the energy of stretching. This liberated heat would partially neutralize the cooling effect. But when rubber is allowed to retract reversibly under load, the van der Waals joints would have to perform external work, and no heat would be released by them, and hence the cooling effect would be greater. Indeed this larger cooling effect under loaded retraction (adiabatic) has also been predicted on thermodynamic grounds by Gerke.⁹

Factors Controlling *cis* and *trans* Addition

In certain plants, natural processes seem able to lay down molecules of rubber, in others, molecules of gutta, with the C_2H_4 groups in rubber largely or wholly *cis*, and in gutta *trans*. In synthetic rubbers, however, mixtures of *cis* and *trans* configurations result. We may discuss the factors which determine *cis* and *trans* addition in polymerization, taking butadiene as an illustration.

Butadiene is a flat molecule. All of its atomic nuclei, 4C and 6H, lie in a single plane. A scale drawing of the model is given in Fig. 9. There is a double bond between C_1 and C_2 and also between C_3 and C_4 . Between C_2 and C_3 the bond is single. Free rotation can unquestionably occur about this single bond, C_2-C_3 , in the butadiene molecule. But when butadiene polymerizes by end union, the bond between C_2 and C_3 becomes a double bond (and of course C_1-C_2 and C_3-C_4 become single bonds) and thereafter no rotation whatever can take place on the double bond $C_2=C_3$.

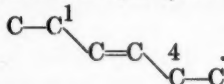
Let us suppose that in the butadiene molecule, either one of the C_2H_3 groups, or both, happens to be rotating or oscillating rapidly about the single bond C_2-C_3 . If, then, at any particular instant the electron bond shift between the various atoms is ready to occur, it will not occur at any and all phases of the bond rotation, but only within the narrow range of phase in which all four carbon atoms happen to be exactly, or nearly, *in the same plane* (since the four carbon atoms of the polymerized molecule also lie in a single plane). There are apparently two such phase instants, the one shown in Fig. 9, and one which is a half revolution, 180° , different. As a matter of fact, however, while the two C_2H_3 groups can lie as shown in Fig. 9, they *cannot* rotate into the other position 180° apart because of the bumping of hydrogen atom H'_4 against hydrogen atom H_1 and the almost simultaneous bumping of hydrogen atom H_3 against hydrogen atom H_2 . The possible rotation is through an angle of only about 145° instead of 180° , and thus fails by about 35° of bringing all four carbon atoms (or the fourth carbon atom) into the single plane.

Both of these configurations of the two halves of the butadiene molecule, the one shown in Fig. 9 and the one 145° different, have a decided preferential existence, as

compared with the other phase configurations. The reason for this is that in these two positions the best hydrogen-to-hydrogen contacts are made. In Fig. 9, there is a contact between H_2 and H'_1 and between H_1 and H_3 ; in the 145° position there is contact, as we have already indicated, between H'_1 and H_1 and between H_3 and H_2 . In other words, *van der Waals forces, operating within the molecule, determine the most probable configurations.* To knock the two halves of the molecule out of these favored positions, and set them into oscillation, would require the action of fairly violent thermal agitation.

Now, if the bond shift occurs when the configuration is that of Fig. 9, the two carbon atoms C_1 and C_4 are in the *trans* positions across $C_2=C_3$, and when end union

occurs, the two C_2H_4 groups are *trans*, thus



On the other

hand, if the bond shift occurs during the 145° configuration, then C_1 and C_4 are *cis*. However, while the chance of existence of the two configurations of butadiene is probably about 50:50, the ease with which the configuration of Fig. 9 polymerizes is considerably greater. The 145° configuration must probably wait for thermal agitation to drive the C_2H_3 group simultaneously through approximately 35° into the plane. It is difficult to evaluate the relative probabilities of formation of the *trans* and *cis* products. The proportion of *trans* to *cis* might be 55:45, 75:25, or 95:5. At any rate, it is fairly certain that the *trans* form would predominate.

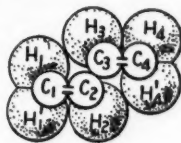
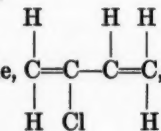
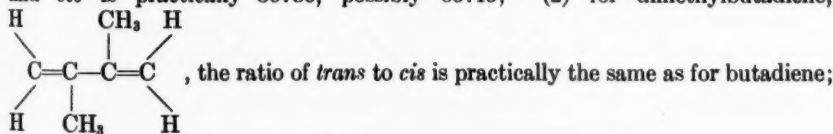


Figure 9

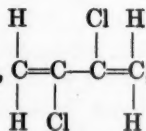
We need not carry through similar demonstrations here for the other substances which may be polymerized to produce rubber-like materials. It can readily be shown with scale models, using the same

geometrical principles, that: (1) for isoprene, $\begin{array}{c} H & & H & & H \\ & \diagdown & & \diagup & \\ C=C & -C- & C=C \\ & \diagup & & \diagdown & \\ H & CH_3 & & H \end{array}$, the ratio of *trans*

and *cis* is practically 50:50, possibly 60:40; (2) for dimethylbutadiene,



(3) for chloroprene, $\begin{array}{c} H & & H & & H \\ & \diagdown & & \diagup & \\ C=C & -C- & C=C \\ & \diagup & & \diagdown & \\ H & Cl & & H \end{array}$, the ratio of *trans* to *cis* is probably about 60:40,



as in isoprene; (4) for dichlorobutadiene, $\begin{array}{c} H & & Cl & & H \\ & \diagdown & & \diagup & \\ C=C & -C- & C=C \\ & \diagup & & \diagdown & \\ H & Cl & & H \end{array}$, the ratio of *trans* to *cis* is

possibly about 40:60; that is, the *cis* predominates. This prediction is made on the basis that not only are the two halves of the molecule more nearly in the same plane when Cl touches Cl and H touches H, but also because the van der Waals attraction between Cl and Cl is probably so much greater than between Cl and H,

that the *cis* position giving the van der Waals contacts $\text{Cl} \cdots \text{Cl}$ and $\text{H} \cdots \text{H}$ is almost certainly more favored than the *trans* position giving the van der Waals contacts $\text{Cl} \cdots \text{H}$ and $\text{Cl} \cdots \text{H}$.

Properties of Synthetic Rubber

Finally, it might be interesting to predict the properties of the various synthetic rubbers, on the basis of the foregoing theory. The matching of prediction against fact cannot be very satisfyingly specific and detailed both because of the only semi-quantitative character of our theory and because of the obscurity of the facts and spread in the claims and contentions made by various investigators in connection with the properties of their products.

Butadiene Rubber.—In butadiene rubber the A group does not rotate through 40° , since there is no CH_3 group beneath it, but only a single hydrogen atom. The contacts between a_1 and a'_1 and the single hydrogen, in Fig. 10, are *two*, and are not improved, but spoiled, by rotation. Group B rotates through about 80° , either clockwise or counter-clockwise, to establish *one* more hydrogen contact, as shown in the figure. (Of course, B could equally well remain fixed in retracted form and A rotate through 80° , but both A and B would not rotate, because the best contacting is achieved if one remains fixed.) With a gain of only one hydrogen contact per double bond, the work of stretching this rubber would therefore be small. The retractive mechanism functions only when the two C_2H_4 groups are *cis*, and thus with a preponderant population of *trans* configurations along the polymerized chain, the work of stretching and the

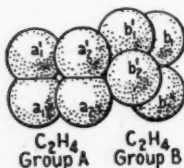
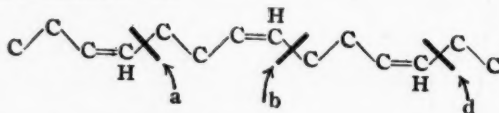


Figure 10

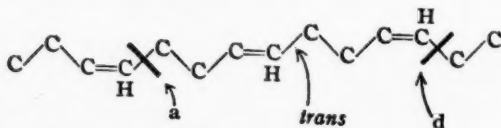
retractive power become still further reduced.

This sacrifice of strength at the *trans* configurations is accompanied however by a gain in elongation. If the butadiene rubber were composed entirely of *cis* configurations, as in the first formula below, it would have substantially the same elongation as the molecule of natural rubber, about 3, previously suggested. Let us make this point clear by means of carbon chain formulas.

cis-butadiene-rubber



cis- and *trans*-butadiene-rubber



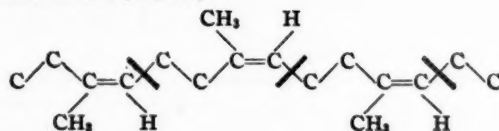
In the *cis*-rubber the C_2H_5 links rotate about the *Cis* planes, *a*, *b*, and *d*, as shown in the formula. (*Cis* is capitalized to distinguish the relationship across the ends of a C_2H_5 group from that across >C=C<). The interposition of the *trans* bonding between the two *a* and *d* rotation planes, which then become *Cis* with respect to each other, as shown in the synthetic rubber formula, produces a profound change in the shape possibilities for the molecule. (1) Not only is the link from *a* to *d* twice as long as the normal link, but (2) the non-compulsory rotation of the *trans*

bond, which may occur because of crowding by neighbor groups and neighbor molecules, is *Trans* with respect to a and *Cis* with respect to d. Both of these features result in allowing the molecule to twist its links much more frequently into a closely packed folded chain, and hence may increase greatly the elongation of the average molecule, and hence also of the rubber.

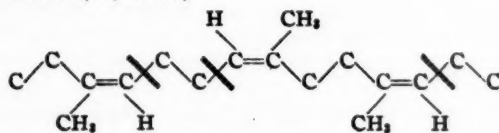
It should be noted, finally, that the proportion of junk material, partially polymerized molecules, is certain to be far greater in butadiene than in natural rubber.

Isoprene Rubber.—The properties of this rubber would be the same as natural rubber, except for the more abundant junk molecules, and except for the preponderance of *trans* configuration, in which case, as we have previously pointed out, the 100° rotation of the B group does not function. The elongation may well be greater than in natural rubber because of inversion.

Not inverted (*cis, Cis*)



Inverted (*cis, Trans*)



In the non-inverted *cis* C_2H_4 type, the regular 100° group B rotation occurs across the ends of C_5H_8 links, and is *Cis*. But in the inverted, *cis* C_2H_4 type, this rotation occurs across the ends of short links, C_2H_4 , and long C_8H_{12} links, interspersed, and is *Trans*. In the above structures the planes of rotation are indicated by heavy slanting lines. It is perhaps obvious from these structures, and is easily demonstrated with models, that inversion develops different shape possibilities for the retracted rubber molecule, and very decidedly improves the chances of spiraling and more compact zig-zagging.

Dimethylbutadiene Rubber.—Here both C_2H_4 groups function as A groups, whether they are *cis* or *trans*, rotating through 40° . There is a chance of one-half that they will turn toward one another, that is, one clockwise and the other counter-clockwise, and also a probability of one-half that they will not turn toward one another, that is, both clockwise or both counter-clockwise. In the former case the molecule becomes considerably shortened, and consequently acquires a fairly large elongation; in the latter case, the elongation is extremely small, only about as large as in a gutta molecule. The average elongation behavior, then, for a rubber matrix could be readily predicted. The work of stretching would be large, since all of the C_2H_4 groups function, and every one establishes two more hydrogen contacts in retraction. No inversion is possible. The junk factor, of course, must be considered.

One further point should be noted. The introduction of two C_2H_4 groups, whether *cis* or *trans*, on to $>C=C<$, together with two CH_3 groups, crowds these groups together very severely, particularly when groups A and B are unwound into extended form. In fact, it is only because of the possibility of some bond bending, and the "mashing" in of the hydrogen atom domain¹⁰ that the structure, especially

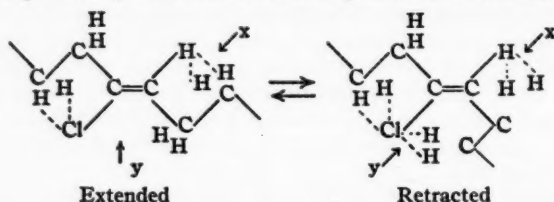
in extended form, can exist. It would be natural to expect, then, that this rubber would be sluggish in retraction, but that its "snap" would improve at higher temperatures, with the assistance of increased thermal agitation. Whitby and Katz say:¹¹ "It was observed that, when warmed, the specimens of methyl rubber largely lost their sluggishness."

Dichlorobutadiene Rubber (?).—In this polymerized product the C_2H_4 groups, whether *cis* or *trans*, are not crowded by the two chlorine atoms, as they are by CH_3 groups in methyl rubber. The product, however, should *not* possess any rubber-like properties, and should not be called rubber at all. Both C_2H_4 groups, whether *cis* or *trans*, are rigidly locked in extended position, each by contacts between two hydrogen atoms and a chlorine atom. No rotation of either group A or group B would be possible.

Chloroprene Rubber.—In the case of chloroprene rubber we are in the fortunate situation of possessing a fairly abundant mass of facts, much less obscure than in the case of other synthetic rubbers, supplied in the main in the brilliant original paper of Carothers,¹² Williams, Collins, and Kirby.

When the C_2H_4 group B, in α -polychloroprene, or in μ -polychloroprene, is *cis* with respect to group A, it functions exactly as in butadiene rubber: the angle of rotation is again about 80° , and the magnitude of the van der Waals retractive force is probably essentially the same. The only difference in the entire situation is that group A is held much more firmly in its extended position (non-rotating) by the Cl atom than it is in butadiene rubber by the hydrogen atom. This, however, makes no difference in the general result, as long as group B is free to execute its 80° rotation, as it is.

When group B is *trans* to A it also functions as retractive mechanism. The geometry of the arrangement can best be demonstrated with scale models, but the effect may be explained by means of the following structural formulas.



In the extended form two good hydrogen contacts occur at x, but none at y between the Cl and the two hydrogens of group B. But in the retracted form, involving a rotation of group B through 180° , possibly accompanied by a small rotation on bond 2 of group B, not only is the hydrogen contacting at x just as good as before, but additional contacts are made between two hydrogen atoms of group B and the Cl atom at y. (Internuclear distance C—H is 1.08 Å. U., C—Cl is 1.91 Å. U.; domain radius of H is 1.29 Å. U., of Cl is 1.51 Å. U., at room temperature.) The van der Waals attraction between Cl and H is very much stronger than the attraction between H and H. This is clearly indicated by a comparison of the boiling points for CH_4 , $CHCl_3$, CH_2Cl_2 , CCl_4 , and other chlorinated hydrocarbon molecules. It would not be difficult to calculate empirically the work of extension of this *trans* Cl H "joint," in the same manner as done previously for the retraction mechanism in natural rubber. But we shall be content with this qualitative demonstration. The work of stretching would be large.

There is every reason to believe that there are irregularities along the chains of α - and μ -polychloroprene, that is, both inversion and a mixture of *cis* and *trans*

configurations,¹³ the latter in a proportion something like that predicted in the previous section on polymerization to *cis* and *trans* forms. These irregularities would lead to a large elongation, as suggested previously.

Since polychloroprene polymerizes extremely rapidly, relatively, there should be very little junk material present, when the rubber is recovered. The Joule effect should appear, that is, some of the C_2H_4B groups should freeze, upon stretching, at least those of the *x*-molecules, oriented initially near the direction of stretch, and possibly only the *cis* B groups, because their retractive pull is less than that of the *trans* B groups.

A future discussion of the factors involved in vulcanization, and perhaps also a discussion of the catalysis of polymerization, are contemplated.

It is a pleasure to acknowledge assistance from Thomas Midgley, Jr., Albert L. Henne, and Alvin F. Shepard. I am also particularly grateful to my colleague, Preston M. Harris, for many helpful suggestions and criticisms.

Summary

A theory of the mechanism of elastic stretch in rubber is described. It is christened a "hydrogen-evaporation-condensation" mechanism. In an attempt to develop a unified theory of rubber behavior, some of the more important properties of the various forms of rubber are discussed, from the point of view of strict adherence to the principles of geometry and of structural organic chemistry. Among the topics discussed are: shape of the rubber molecule, the work of stretching rubber, the shape of the stress-strain curve, heat effects in rubber (including the Joule effect), Staudinger's hydrogenated rubber, factors controlling *cis* and *trans* addition, x-ray diffraction pattern, properties of synthetic rubbers, inversion, and sluggishness.

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- ⁹ Gerke, *Ind. Eng. Chem.*, **22**, 73 (1930).
- ¹⁰ In the models employed, the hydrogen atom is assumed to possess spherical symmetry, at least in its outer domain, like other atoms. The hard spherical surface of its electron domain (merely a token for the equilibrium distance of approach between hydrogen nuclei) may however be invaded by another atom making a sufficiently violent impact. In this sense the domain may be penetrated, or distorted, or "mashed" in from the room-temperature equilibrium radius of 1.29 A. U. to perhaps about 1.0 A. U. (see Ref. 5).
- ¹¹ In this paper the C=C internuclear distance has been taken as about 1.45 A. U., instead of a possibly more probable smaller value, more like the 1.2 A. U. used by Meyer and Mark, "Der Aufbau der Hochpolymeren Organischen Naturstoffe," Akademische Verlagsgesellschaft, Leipzig, 1930, pp. 189-206. This was done to facilitate the two-dimensional representation of the models in the drawings, and to allow me to avoid discussion of the hydrogen domain penetration. The difference is small, and does not disturb the qualitative or the semi-quantitative aspects of the present theory.
- ¹² Whitby and Katz, *Can. J. Research*, **6**, 398 (1932); *RUBBER CHEM. AND TECH.*, **5**, 566 (1932).
- ¹³ Carothers, Williams, Collins, and Kirby, *J. Am. Chem. Soc.*, **53**, 4203 (1931).
- ¹⁴ It is probably not permissible for Carothers, Williams, Collins, and Kirby (Ref. 12) to draw the conclusion, from their x-ray diffraction pattern (their Fig. 1), that "the polychloroprene is freer from irregularities in the structure of its molecules than other synthetic rubbers." In the first place, the absence of sharp x-ray patterns in the case of other synthetic rubbers is to be partly accounted for in terms of the abundant junk materials present, as well as in terms of irregularities. In the second place, their x-ray diagram is far from being "sharp." Its spots are quite diffuse.

Vulcanization and Stress-Strain Behavior of Sol, Gel, and Total Rubber Hydrocarbon

W. Harold Smith and William L. Holt

NATIONAL BUREAU OF STANDARDS, WASHINGTON, D. C.

1. Introduction

The existence and significance of a soluble and an insoluble fraction in rubber hydrocarbon and the proportions in which they occur have long been the subject of conflicting reports, which have been summarized in a previous paper.¹ They were the basis of a two-phase theory of rubber structure proposed by Fessenden.² The history of the subject need not be reviewed here. Early knowledge of it was summarized by Engler and Herbst³ in 1887 and an excellent historical treatment has been given by Whitby.⁴

The differing solubilities and other characteristics of the two fractions suggested a study of their behavior when vulcanized. A sufficient quantity of rubber hydrocarbon for the purpose was purified and separated into the soluble and insoluble fractions by extraction with ethyl ether; suitable compounds of each were mixed and vulcanized, and comparative tests made.

2. Preparation of Fractions

Purified rubber hydrocarbon was obtained from the latex of *Hevea brasiliensis* by a method previously described in this journal.⁵ The main purpose of the method of purification was to separate the fractions as sharply as possible while maintaining the structure of the rubber hydrocarbon as it exists in the latex. The purified hydrocarbon was separated into two fractions by thorough, continuous extraction with ethyl ether for several days. A stream of nitrogen was used to displace oxygen in the ether and a little phenyl- β -naphthylamine, a commercial antioxidant, was added to the ether from time to time during the separation of the fractions. The soluble fraction constitutes approximately 75 per cent of the total rubber hydrocarbon, and the insoluble or gel fraction, 25 per cent. The separated rubber fractions were desolvated by acetone, and the residual acetone and ether were removed from the rubber *in vacuo*. A little of the phenyl- β -naphthylamine which was in the ether during extraction remained in the rubber hydrocarbon, and, after the removal of the acetone and ether, an additional 1 per cent of it was milled into each fraction. Whenever it was necessary to preserve the fractions, they were kept in a desiccator filled with nitrogen.

3. Vulcanization of the Fractions and Results of Tests

Before the fractions of rubber hydrocarbon were vulcanized, the possible effect of ethyl ether, not completely removed, was determined with pale crepe. Solvents have a softening action and change the physical properties of vulcanized compounds. A sample of pale crepe was allowed to remain in contact with ether until the soluble fraction formed a very viscous solution. The ether was then removed *in vacuo*, and the residual rubber and a sample of the original pale crepe were compounded as follows:

Ingredients	Parts by Weight
Pale crepe	100
Sulfur	3
Zinc oxide	5
Diphenylguanidine	1
Stearic acid	0.75

Samples were vulcanized simultaneously for 20 and also for 30 minutes at 142° C. For each cure, the stress-strain properties of compounds representing rubber treated and untreated with ether were alike to 600 per cent elongation. There were slight but negligible differences at higher elongations. It was evident that, for the purposes of this work, the use of ether in separating the fractions did not cause differences in tensile characteristics such as are indicated in Fig. 1.

Preliminary work on the behavior of the fractions when vulcanized was carried out with a compound containing tetramethylthiuram disulfide, a rapid accelerator of vulcanization. A small quantity of compound containing each fraction was mixed on a laboratory mill and vulcanized in the form of rings. Tests of the vulcanized soluble fraction indicated a modulus, at 500 per cent elongation, of 500 lbs. per sq. in. The modulus of the vulcanized insoluble fraction at the same elongation was 250 lbs. per sq. in. The insoluble (gel) fraction produced a much stiffer compound than the soluble (sol) fraction.

It appeared desirable to use a slow accelerator of vulcanization to accentuate any differences in the fractions through the greater divergences of the stress-strain properties. Triphenylguanidine was chosen, and the following compound was used:

Ingredients	Parts by Weight
Rubber	100
Sulfur	3
Zinc oxide	5
Stearic acid	1
Triphenylguanidine	2
Phenyl- β -naphthylamine	1

Three lots were prepared, one containing the soluble fraction, the second the insoluble or gel fraction, and the third for comparison contained total rubber hydrocarbon. The total hydrocarbon was purified by the method⁶ which has been described, but was not separated into fractions.

The compounds were mixed in lots of about 50 grams each by careful manipulation on a small laboratory mill. While mixing, it was quite evident that a difference existed between the two fractions. The insoluble or gel fraction as distinguished from the other rubbers was difficult to "break down" or plasticize on the mill, and the resulting compound retained a gristle-like character. Compounds were vulcanized in sheets 2 by 4 inches and about 0.040 inch thick, from which dumb-bell specimens were cut out for test purposes. Three periods of vulcanization were used, *viz.*, 50, 70, and 100 minutes, respectively, at 142° C. Stress-strain results obtained with each compound are shown in Fig. 1.

At each period of vulcanization the compound containing the soluble fraction is more extensible than that containing the insoluble, and the total hydrocarbon has an intermediate position. As the total hydrocarbon consists of 75 per cent soluble and 25 per cent insoluble rubber, the stress-strain curves of the compounds made with total rubber are closer to those containing the soluble fractions than to those containing the insoluble fractions. The stress-strain behavior of the total rubber is therefore in accord with the relative proportions of the two fractions present in it.

Samples of each fraction and of the total rubber hydrocarbon were pressed into thin sheets and vulcanized at room temperature by the Peachey process,⁷ in which vulcanization is effected by nascent sulfur obtained by the interaction of hydrogen sulfide and sulfur dioxide. As might be expected from previous experience, it was difficult to obtain satisfactory sheets of the insoluble (gel) rubber because of its gristle-like character in the unvulcanized condition. However, some fairly uniform sheets were obtained. The sheets were vulcanized simultaneously and contained

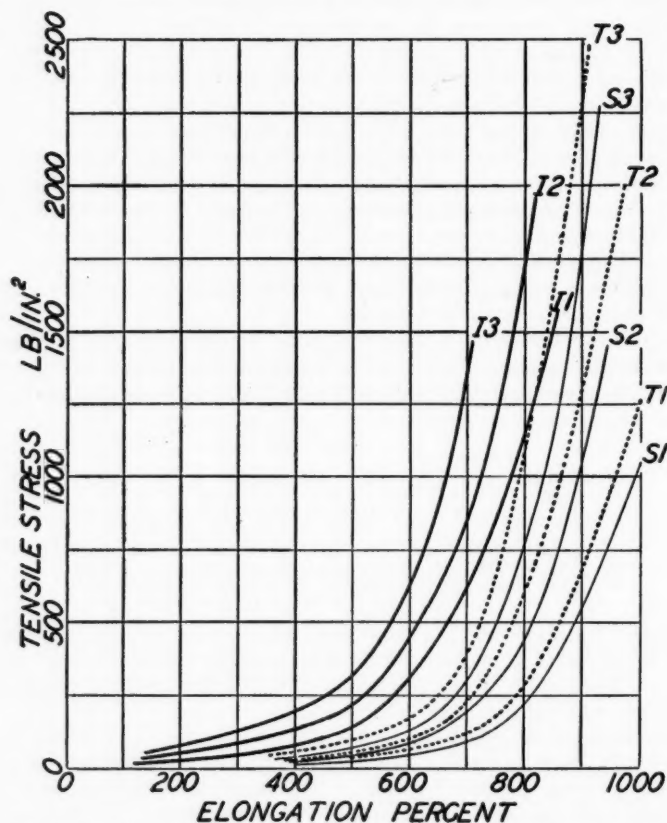


Figure 1—Stress-Strain Curves of Soluble (S), Insoluble (I), and Total (T) Rubbers

Numerals 1, 2, and 3 indicate short, medium, and long cures, respectively.

approximately 0.4 per cent (see Table I) of combined sulfur, which represents a light cure. Stress-strain data of ring specimens exhibited a behavior similar to that shown in the graph. The gel rubber was the less extensible fraction, the sol rubber was the more extensible, and the curve representing the total rubber occupied a position intermediate between those representing the fractions.

The amount of combined sulfur was found by analysis in samples of all compounds used in determining stress-strain data. The results obtained are given in Table I.

TABLE I
RESULTS OF THE DETERMINATION OF "COMBINED" SULFUR IN SAMPLES OF THE VULCANIZED RUBBERS

Percentage of Sulfur in the Vulcanized Rubbers Prepared from—			Conditions of Curing		Accelerators Used in Vulcanizing
Soluble Rubber Hydrocarbon	Insoluble Rubber Hydrocarbon	Total Rubber Hydrocarbon	Temperature, ° C.	Time, Min.	
1.94	1.84	1.96	126	30	Tetramethylthiuram disulfide
1.35	1.34	1.21	142	50	
1.57	1.64	1.45	142	70	Triphenylguanidine
1.91	2.04	1.81	142	100	
0.33	0.47	0.35	Vulcanized by Peachey process

From these it appears that differences in the stress-strain behavior of the fractions and the total rubber were not caused by varying amounts of combined sulfur, but must have been due to differences in the rubber, which persisted through vulcanization.

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- ¹ *Bur. Standards J. Research*, **10**, 479 (1933); RP 544.
- ² *Science*, **20**, 52 (1892).
- ³ *Ladenburg's Handwörterbuch der Chem.*, **5**, 479 (1887).
- ⁴ *Colwyn Medal Essay, Trans. Inst. Rubber Ind.*, **6**, 42 (1930-31).
- ⁵ See footnote 1.
- ⁶ See footnote 1.
- ⁷ *Ind. Rubber J.*, **63**, 427 (1922).

Ether-Insoluble or Gel Rubber Hydrocarbon, Its Solution, Crystallization, and Properties

W. Harold Smith and Charles Proffer Saylor

NATIONAL BUREAU OF STANDARDS, WASHINGTON, D. C.

I. Preparation and Crystallization of Gel Rubber Hydrocarbon

W. Harold Smith

1. Preparation of the Gel

A method of purifying and crystallizing ether-soluble rubber hydrocarbon was described in an earlier paper in this journal.¹ The same procedure for purifying the hydrocarbon and separating it into two fractions was followed in the preparation of the insoluble or gel fraction, the properties of which are the subject of this paper. The method of purification was not merely another procedure for removing the impurities from rubber hydrocarbon, but, as stated in the earlier paper, it also "sought to maintain unchanged the structure of rubber hydrocarbon and to permit a sharp separation of the ether-soluble and insoluble fractions."

The latex which has been used was, in part, obtained from H. L. Fisher of the United States Rubber Co. Through the courtesy of the U. S. Department of Agriculture, latex has also been obtained direct from the plantation on the north shore of Haiti. Before the trees were tapped, the area surrounding the intended incision was carefully cleaned. After tapping commenced, the trees were tapped once each day, the latex from the first two tappings was rejected, and that obtained on the third day was put into clean glass bottles, which were filled completely after the addition of a little ammonia as stabilizer. The latex was immediately shipped to this Bureau and stored at a temperature maintained between 0° and 2° C.

Briefly, the rubber hydrocarbon was prepared as follows. Latex of *Hevea brasiliensis* was dialyzed and the protein removed by tryptic digestion in the presence of natural antioxidants, which had been extracted from crude rubber and which were added to the latex at intervals. The purified hydrocarbon was separated into two fractions by thorough continuous extraction with ethyl ether in an apparatus constructed entirely of glass and similar to that described by Pummerer, Andriessen, and Gündel.² Oxygen in the apparatus was displaced by a continuous stream of nitrogen of 99.8 to 99.9 per cent purity. The nitrogen was under slight pressure, and to facilitate the exclusion of air all joints were covered with a film of glycerol. The rigid exclusion of oxygen is necessary because the presence of even a minute amount of it causes the gel to dissolve slowly and makes a sharp separation impossible. It is advantageous to have an antioxidant in the solution during the extraction, and either the natural antioxidants or phenyl- β -naphthylamine was used. With these precautions against oxidation, it was possible to separate the rubber into the two fractions rather sharply.

The manner in which oxygen causes the insoluble gel fraction to become soluble is not understood. Oxygen adsorbed by the rubber, or a trace of an oxygen addition product of rubber such as that formed by autooxidation, or a trace of acid

formed by oxidation may peptize the gel in suitable organic solvents. In a typical experiment with 50 grams of total rubber the extraction was continued beyond the point at which it is normally considered to be complete. One week of continuous extraction was required. The final extract was removed, a fresh supply of ether, which had been previously saturated with nitrogen, was added to the rubber, and the extraction was continued for 72 hours longer. The extract contained 20 mg. of rubber, or 0.04 per cent of the original sample. The swollen gel rubber which remained after extraction was desolvated with acetone, and residual ether and acetone were removed *in vacuo*. If it was necessary to preserve the gel fraction for an interval, it was cut into suitable small pieces and allowed to remain for 24 hours in an acetone solution of the natural antioxidants or of phenyl- β -naphthylamine. The acetone was removed *in vacuo*, and the gel was placed in a desiccator which was evacuated and filled with nitrogen several times. Before the gel was put to any use, the antioxidants were removed by extraction with acetone.

In the extraction of numerous samples of latex, about the same proportion of gel, 25 per cent of the original hydrocarbon, was always obtained. Other observers have reported very divergent proportions, ranging from 0 to 70 per cent, in rubber of various kinds extracted with different solvents.

The quantitative determination of sol and gel in the total rubber by extraction with ether must be conducted in the absence of oxygen. A small Soxhlet extractor, suitably modified to allow a continuous stream of nitrogen to pass through it during the extraction, was used. The upper outlet of the extractor, above the condenser, was connected to a flask through which an auxiliary stream of nitrogen was constantly passed and the outlet of the flask consisted of a mercury bubble trap. To avoid prolonged extraction, samples weighing about 1 gram were used. They were first extracted with acetone to remove antioxidants and the weight of the sample was corrected for acetone-soluble material. After the excess acetone was siphoned from the rubber, ether was added to remove residual acetone and immediately siphoned away. Sufficient ether was added to cover the rubber, the flask was cleaned and filled with ether, the apparatus assembled, and nitrogen was passed through it. The rubber was allowed to swell to a maximum before the extraction with ether was started. During the extraction, fragments of the swollen gel tended to become detached and to be swept out with the extracted material. The rubber was therefore placed in a container of no. 100 platinum gauze of sufficient size to permit the rubber to swell to its maximum volume. The approximate time necessary to extract the soluble fraction was determined on a separate sample by weighing successive extracts. The last traces of soluble material were removed with difficulty from the swollen gel. When the extraction was complete the ether was removed from each fraction *in vacuo* and the residues were dried *in vacuo* to constant weight. Each fraction was corrected for ash.

The mean of six determinations, which were obtained after some familiarity with the details of the method was acquired, indicated a sol content of 75.3 ± 0.8 per cent and a gel content of 24.2 ± 0.7 per cent. Probably a little gel was dissolved during the extraction and the results represent only an approach to the true value.

2. Some Properties of Sol and Gel

Some investigators who purified rubber by methods other than the one which is used in this work, noted differences in the soluble and insoluble fractions. The fractions of rubber, as separated in this investigation, show marked differences. The sol can be stretched or otherwise deformed more than the gel and by smaller forces, and it can be readily masticated on a rubber mill. The gel is tough, resistant

to mastication, and may be described as gristly. No quantitative study of the physical properties of the unvulcanized fractions has yet been made.

A sol-gel reversible transformation has been attributed to rubber on the assumption that a single chemical compound is concerned. The data which follow on the melting points of crystals obtained from the gel after it has become soluble in ether indicate that the soluble gel is not the same hydrocarbon that is in the ether-soluble fraction of total rubber hydrocarbon. Consequently the gel and sol, as these terms are here used, are not merely different phases of the same molecular species.

Porritt³ observed that gel was formed in a rubber solution which was sealed in glass and exposed to sunlight. When the container was opened the gel became soluble. A similar effect in a solution of ether-soluble rubber has been noted by the author. (See footnote 1.) There is no evidence that the gel formed in the sealed tube is identical with that left after the original extraction of the rubber with ether. The conversion of the sol to a gel has not yet been investigated by an examination of the crystals.

3. Dissolving and Crystallizing the Gel

The gel was dissolved in an organic solvent by permitting the entry of a little air and, depending upon the amount of air used, temperature and other conditions, the time required completely to dissolve the gel could be varied from a few weeks to several months. Ethyl ether, ethylbenzene, or toluene was generally used because it remains liquid under the conditions of crystallization. Inorganic components of the latex, which concentrate in the gel when the soluble fraction is extracted, remain undissolved by the organic solvent.

It is evident from the preceding discussion that the gel fraction is separated from the sol by its insolubility in ethyl ether and that subsequently it is dissolved in ethyl ether. Organic compounds of high molecular weight tend to be less soluble in the inert solvents than their simpler homologs. The solution of the gel probably contains the products of disaggregation of a more complex structure which exists in the insoluble gel.

Suitable conditions for the growth of crystal nuclei of ether-soluble rubber hydrocarbon and the establishment of their crystal habit were discussed in the earlier paper. (See footnote 1.) The same technic was used to obtain crystals of the dissolved gel fraction. When hydrocarbon solvents were used, they were customarily diluted with anhydrous ethyl ether before crystallization of the rubber, as this medium has greater fluidity and therefore insures greater mobility of the nuclei than hydrocarbon solvents alone. One volume of a hydrocarbon solution of rubber diluted with four volumes of ethyl ether is suitable, but these proportions may be varied considerably. For studies of the optical properties and melting point, the dissolved gel hydrocarbon was crystallized from ethyl ether or a mixture of ethylbenzene and ethyl ether.

The particles which appeared in the solution at low temperature were birefringent under crossed nicols, and nodules formed on the walls of the container when proper supersaturation existed in the solution, a behavior similar to that observed with ether-soluble rubber hydrocarbon. Between 90 and 95 per cent of the rubber in the solution separated as crystals.

The optical properties of the crystals were studied with deposits made in the special cell which was described in the earlier paper. (See footnote 1.) The following technic was developed to permit the study of several crystalline deposits obtained simultaneously from a single solution. A vertical glass support was provided with glass brackets to hold a succession of cover glasses and the support was placed in a 12-in. test tube which contained the solution of gel rubber. Two cover

glasses were placed on each bracket to prevent the deposition of crystals on the under side of the upper cover glass—the one which was subsequently observed. After crystallization was accomplished the ethereal solution was removed at low temperature through a siphon and the crystals were washed with acetone at a temperature below the melting points of the crystals, and the acetone was then similarly removed. After washing with cold acetone several times, a cold solution of calcium chloride was poured into the tube. A cover glass was quickly removed from the rack when required and placed in a cold solution of calcium chloride under the objective of a microscope.

A supplementary method of obtaining crystalline rubber has been observed. If a lump of pure sol rubber, or of gel rubber which previously has been made soluble, is placed in cold ether and the temperature maintained at -55° to -60° C., crystals are produced. The solubility under these conditions is sufficient to permit a continuous deposition of crystalline hydrocarbon. This technic is commonly used by the crystallographer and it may offer a means of producing crystalline rubber in greater quantity than can be readily obtained from previously prepared solutions. Aside from establishing the crystallinity of the deposits by their appearance when viewed between crossed nicols, no detailed study of their optical properties was made.

The effect of a trace of trichloroacetic acid or of a mineral acid in a solution of total rubber is well known to rubber chemists. The viscosity of the solution is lowered and a profound change occurs in the structure of the rubber. Sunlight accelerates these changes. Gel rubber hydrocarbon was dissolved in ethylbenzene which contained 0.05 per cent of trichloroacetic acid. When it was completely dissolved the acid was removed, and the rubber hydrocarbon in a solution of suitable concentration was subjected to the conditions for obtaining crystals. A deposit was obtained which was found to be crystalline when viewed between crossed nicols. The initial products of disaggregation can therefore be crystallized.

4. Composition of the Gel Crystals

Crystalline hydrocarbon obtained from the dissolved gel fraction was analyzed by H. J. Wing to determine the ratio of hydrogen to carbon. The apparatus described in *Research Paper* RP 544 was used, and the ratio was established by the criteria discussed in that paper. It was necessary to heat carefully when removing traces of solvents from the rubber. To effect this, the sample was placed in a small glass chamber and heated to 100° C. by a glycerol bath. A low pressure was maintained by a mercury vapor pump. It was observed that the ether-insoluble material obtained by crystallization was more susceptible to decomposition, as indicated by discoloration and an odor of oxidation products, than ether-soluble rubber obtained similarly. Attempts to prepare suitable material for combustion often failed. However, three determinations were made in which the technic was satisfactory. The ratios of hydrogen to carbon were 0.1346, 0.1346, and 0.1347, respectively, and corresponded to that required by a compound of formula C_5H_8 , on the assumption that the compound does not have more than 100 carbon atoms in the molecule.⁴

It will be observed in the section on the solubility and melting points of the crystals obtained from dissolved gel, that there is continuous melting of the crystals over certain ranges of increasing temperature. This suggests the possible presence of a solid solution. If a solid solution exists in the ether-insoluble fraction before it becomes soluble, the solid solution might consist either of rubber polymers of C_5H_8 of varying complexity; or it might consist wholly or in part of molecular species in which the ratio of hydrogen to carbon differs slightly from C_5H_8 . The

evidence favors the former condition. Should the latter exist, the variation in the composition of the crystals must be very small and it is doubtful whether analyses by combustion can disclose it.

II. Microscopical Study of the Dissolved and Crystallized Gel

Charles Proffer Saylor

1. Habit and Appearance

The same apparatus⁵ as previously described was employed to observe the growth of the crystals and to learn their habit. This apparatus consists essentially of a petrographic microscope, the tube of which is used in an inverted position, a special Dewar flask so constructed that it has plane windows at the bottom, a cell which has plane windows at top and bottom, and tubes for emptying and filling. The cell holds about a milliliter of fluid. In addition to these, there are various structural parts and devices which provide illumination and temperature control. For further details, reference is made to the earlier article.

We frequently watched the crystals in the process of forming by filling the cell with a solution of the gel,⁶ keeping it at -50°C. for about 1 hour, cooling to -70°C. for a few minutes, and then transferring it to the Dewar flask for microscopical examination at low temperatures. Here for several hours it was maintained at approximately -50°C. Finally, when the cell was observed between crossed nicols, bright birefringent particles began to appear. They remained suspended in the fluid and moved with the convection currents, until, growing in size and number, they clustered and settled. Finally, with some amorphous material, they covered the bottom of the cell. The crystalline masses formed in this way were not satisfactory for general observation or the determination of properties. For the purpose of shortening the time necessary to produce crystals the amount of supercooling had been large. Too many nuclei formed, the individual crystals were too small, and the complexity of the groups obscured their component parts.

Better crystals resulted when the apparatus and cycle of temperatures employed for the ether-soluble fraction (reference 1, p. 483-484) were again used. In this procedure the milder supercooling (to -65°C. instead of -70°C.) and the greater freedom from convection currents seem to cause formation of fewer nuclei and therefore fewer and better crystals. Even when this method was closely followed, the crystalline clumps were much less reproducible than were those obtained from the ether-soluble rubber hydrocarbon. Most frequently the nodules were badly ordered groups of birefringent particles, the individual shapes of which could not be discerned. This appearance is represented in figure 1(A). Occasionally, when only a very small part of the rubber in solution had crystallized over a long period, branching groups of needles were obtained. Sometimes there were spherical clusters formed from numerous needles radiating from a center. These, which were rarely obtained, had the same appearance as the crystals of ether-soluble hydrocarbon which were previously illustrated.⁷

2. Optical Properties

A preparation in which the slender crystals radiated from a center was used for the determination of refractive indices. Needles projecting slightly from the group were used for the actual determination because they permitted greater accuracy. The liquids which matched their indices appeared satisfactory for the main body of

the clumps, but the sensitivity was greater with the projecting needles on account of their isolation. The refractive indices at -5°C . for light vibrating parallel and

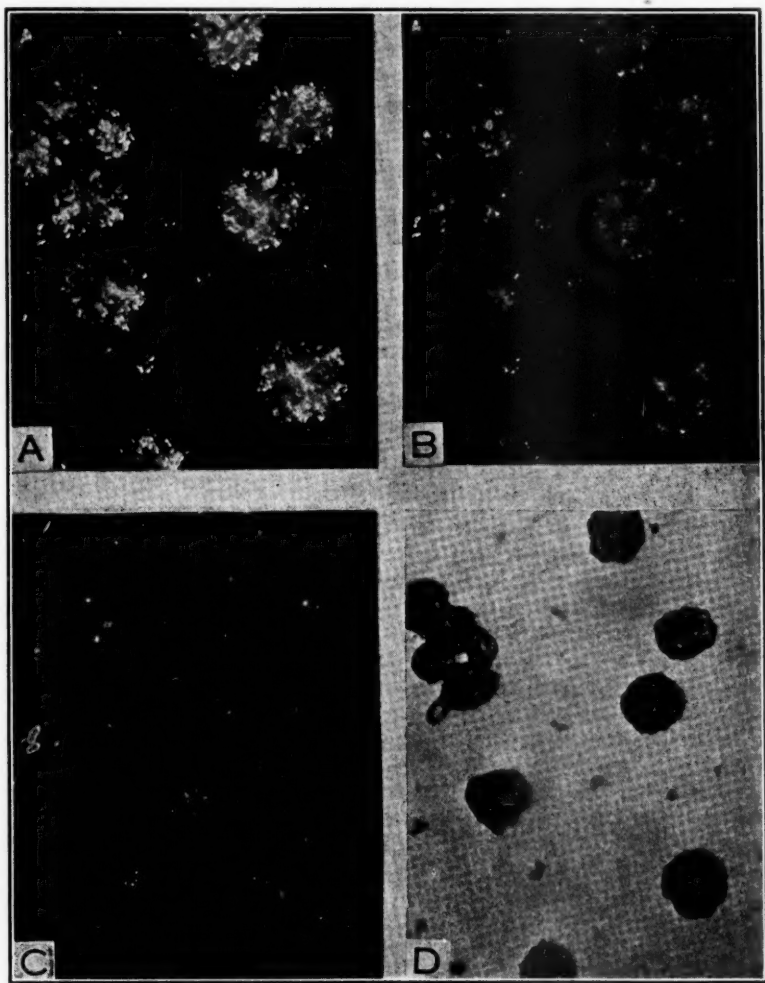


Figure 1—Photomicrographs Showing Melting of One Sample of Gel Rubber Crystals

- A**, Crossed nicols $\times 200$. The mother-liquor has been replaced with acetone and the temperature allowed to rise, but the appearance of the field is not detectably changed. The brightness of the groups is caused by the optical anisotropy of the many crystals which compose them. Temperature, -6.2°C .
B, Crossed nicols $\times 200$. The temperature has risen about four degrees. A large part of the brightness has disappeared, indicating that considerable melting has already occurred. Temperature, -1.9°C .
C, Crossed nicols $\times 200$. Melting is nearly complete. Temperature, -0.4°C .
D, Parallel nicols $\times 200$. After melting, surface tension has shrunk the clusters, but the large part of their structure which remains will continue indefinitely. Temperature, $+0.4^{\circ}\text{C}$.

normal to the long directions of the needles were found by immersion, the method of central illumination serving as a criterion of the relation between the indices of

the crystals and the immersing liquid. The immersion liquids were concentrated aqueous solutions of potassium mercuric iodide, diluted with acetone progressively until the indices of the crystals were matched. An Abbé refractometer was used to determine the indices of the immersion liquids at -5°C . As in the previous paper, and with the same reservations, the index for light vibrating parallel to the long direction of crystals has been designated as ϵ . The values

$$\begin{aligned}\epsilon &= 1.533 \text{ at } -5^{\circ}\text{C}. \\ \omega &= 1.583 \text{ at } -5^{\circ}\text{C}.\end{aligned}$$

were so close to those previously reported for the crystals of ether-soluble hydrocarbon

$$\begin{aligned}\epsilon &= 1.535 \text{ at } -5^{\circ}\text{C}. \\ \omega &= 1.583 \text{ at } -5^{\circ}\text{C}.\end{aligned}$$

as to lie well within the probable error of the determination. The close similarity in the optical properties of the crystals obtained from solutions of the ether-soluble and the gel portions of the rubber does not necessarily indicate identity. Members of the normal paraffins, the normal saturated higher fatty acids, and many other series show similarly close refractivities. Other properties indicate that the two fractions of rubber differ in molecular composition, but it is probable that the molecules are similarly oriented in the crystals of both and that both belong to the same homologous series.

3. Solubility and Melting Point

When crystals of gel rubber in contact either with the ethylbenzene-ether mother liquor or with ether that has replaced it are observed as the temperatures slowly rise from -50°C ., no change is seen until a temperature between -40° and -30°C . is reached. Then through a few degrees the crystals swell with loss of birefringence, and the swollen jelly dissolves at a temperature a degree or so higher. The hydrocarbon has been so changed by or during its solution in ethylbenzene that the form which would not dissolve during continuous extraction with ether for weeks at ordinary temperatures now dissolves quickly at -35°C .

To determine the melting point of the crystals of dissolved gel rubber, many successive preparations were made. The solvent was rinsed out with numerous changes of acetone, and the melting process observed either while the crystals were immersed in acetone or after the acetone had been replaced by ethyl alcohol or a strong aqueous solution of calcium chloride. Melting was determined by the disappearance of birefringence as the temperature was permitted to rise. The melting points as found were entirely discordant. The lack of uniformity persisted when samples were prepared with scrupulous care to make them identical and when the conditions of melting were as nearly as possible the same. For this reason it was necessary to examine larger numbers of samples than was convenient with two cells of the form described. Further, it was desirable to compare the possible effect of environment upon the melting point by employing samples known to be identical, preferably by the use of several portions crystallized simultaneously from the same solution. To do this crystals were grown upon stacks of microscope cover glasses in the way described on page 217 and studied with the simple form of microscope cold stage, illustrated in Fig. 2.

Using this apparatus, in which the temperature rose as the liquid phase in the freezing mixture became diluted, the melting points of different portions from the same crystallization were found to check within a few tenths of a degree. This variation in the recorded temperatures may be explained by difficulties in accurately observing the beginning and end of the slow melting process. The clusters of

needles are complex, which makes it difficult to know exactly when melting begins and when it is entirely ended. The elements of a cluster melt independently. They are protected from one another by the surrounding liquid and by their own resistance to movement after melting. It is possible to observe, therefore, a range of melting not merely for the entire cluster but even for some of the individual crystals of which it is composed. By examining cover glasses upon which crystals had been deposited simultaneously from the same solution, it was found that the crystals of dissolved gel rubber melt at a little lower temperature when they are immersed in acetone than when covered with an aqueous solution of calcium chloride, but that the melting interval is greater when they are immersed in the aqueous

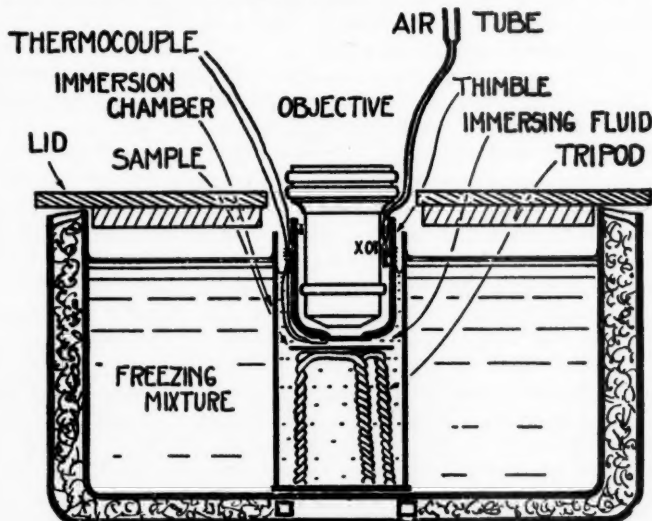


Figure 2—The Simple Cold Stage

Two crystallizing dishes of slightly different sizes were chosen. Except for windows at the center of the bottom, the space between the dishes has been stuffed with rock-wool and the surfaces of the dishes silvered. The dishes are filled with a freezing mixture. Above the windows rests the immersion chamber made from a glass tube to the lower end of which is cemented a glass plate. This contains immersing fluid and a tripod of bent wire upon which the sample rests. The microscope objective dips into the immersing fluid, but is protected by a thimble made from a piece of constricted glass tubing, to the ground lower end of which is cemented a small cover glass. The thermocouple is held in place by being tied with thread to the thimble. The air tube of drawn copper tubing conducts a very slow stream of well-dried air into the space between the objective and the thimble and prevents the formation of frost. The entire apparatus rests upon the stage of a petrographic microscope.

solution. Ethyl alcohol produces intermediate results. It appears from this that although acetone and alcohol are not rubber solvents, small amounts of them are dissolved by the gel rubber at temperatures above its melting point. The melting point observed when the crystals are covered by the aqueous solution must therefore be looked upon as the best value.

When the cells were used they were well drained between applications of liquids. After withdrawing the mother liquor, the crystals were twice treated with acetone, in which they were allowed to steep for several minutes at least. They then received two treatments with aqueous calcium chloride. When the cover glasses were used, they were washed in a stream of cold acetone, steeped in acetone, washed once in aqueous calcium chloride and transferred to another portion of calcium

chloride solution for the melting point determination. The melting point of a preparation treated in this way was the same as the melting point of crystals grown simultaneously from the same solution but with which the steeping in acetone had lasted more than 24 hours. This procedure differs from that described in the paper on ether-soluble rubber hydrocarbon, but the results by the two methods are consonant as indicated by the melting point of 9.7° to 10.3° C. found for sol crystals immersed in aqueous calcium chloride.

Even when the aqueous solution was used to surround the crystals, wide spreads were found between different preparations of crystals.⁸ Sometimes melting began as low as -1.5° C. and at other times not below $+9.6^{\circ}$ C. In a few experiments melting ended at $+5.5^{\circ}$ C. and in others was not complete below $+13.8^{\circ}$ C. There were ranges as great as 8° C. and as small as 1.2° C. The 1.2° C. melting range was exhibited by crystals prepared in the following manner. They were grown in the cell from an ethylbenzene-ether solution. The mother-liquor was removed, the crystals were washed once with very cold ether and dissolved in more ether. From this solution crystals were again grown, the yield being small. The cell was emptied of liquid and filled twice with cold acetone and twice with a cold solution of aqueous calcium chloride. The temperature was allowed to rise and melting was observed from $+4.4^{\circ}$ to $+5.6^{\circ}$ C. Apparently fractionation was produced by the second crystallization from ether. Within the range exhibited by any preparation, the bright spots caused by the birefringence of the individual crystals disappeared sporadically, sometimes with great suddenness. In each cluster the melting was usually continuous, a crystal here and a crystal there losing birefringence without any seeming association. Individual particles sometimes continued to melt over an interval of a degree or more. Neither the melting range of the cluster nor the difference between the melting points of the crystalline particles can be explained by the assumption of delayed equilibrium or of different thermodynamic or chemical environment in the several parts of the clusters. Particles immediately adjacent to one another, separated by less than a hundredth of a millimeter, melted at temperatures differing by 5° or 6° . During the months necessary to dissolve one sample of gel,⁹ crystals made from successive extracts tended to melt at progressively higher temperatures, but the character of the melting (as indicated by length of range and the independence of one another with which the individual particles melted) was the same for all and did not differ from that observed when an entire sample of gel had been dissolved in a single solution. Large irregularities in melting range, which seem to depend only upon the accidents of nucleus formation, persisted and occurred whether the gel had been dissolved in ethylbenzene or in ether. This entire behavior contrasts sharply with that of ether-soluble rubber hydrocarbon, which, when well controlled, always melted at about 10° C.

The way in which dissolved gel rubber crystals melt makes it plain that we are dealing here with no single compound. The gel rubber appears to have dissolved as a result of partial depolymerization. The separate crystals which make the clusters have different molecular compositions and are themselves almost certainly solid solutions of several different polymers. It is obviously desirable that such a mixture be separated into its constituents by fractional crystallization.

4. Elasticity

The simple cold stage illustrated in Fig. 2 made it possible to determine for the sol at least whether the crystals possess the peculiar elasticity of rubber. A striking difference between the properties of the sol and gel fractions was revealed.

Crystals of dissolved gel rubber were grown on microscope cover glasses. One of these was placed in the cold stage under aqueous calcium chloride. The rubber

was present as the entangled network of crystalline needles and rods which is often obtained with the gel. While observing the crystals between crossed nicols they were manipulated with a wire. There was no plastic deformation. Instead the network seemed to yield elastically. The amount and nature of the birefringence did not change, so far as could be noticed. The crystals appeared to be elastic to some degree, but it could not be fully established whether they possessed true rubber-like elasticity. The preparation was allowed to melt and the cover glass taken from the apparatus. The deposit of rubber was pressed into a ball. It had the usual physical properties of gel rubber, considerable stiffness, less extensibility than sol rubber, but also more perfect elasticity.

On the other hand, when a wire was drawn across a preparation of sol crystals, they were found to be plastic. After deformation they had strong birefringence and a new direction of extinction. A clear cover glass was pressed upon the crystalline deposit. The clusters flattened and did not recover when the pressure was released. After some crystals were melted the same experiment with the wire was tried. The rubber could not be plastically deformed, but instead the wire loosened the globules from the cover glass and pushed them aside. The cover glass was taken from the apparatus and washed with water and acetone. The deposit of rubber was rolled into a lump between the fingers. The lump possessed the customary physical characteristics of sol rubber, great extensibility but a rather large permanent set.

5. Comparisons of Sol and Dissolved Gel Rubber

It was made clear on page 215 that gel rubber cannot be dissolved in ethyl ether unless some of the precautions against oxidation are abandoned. Under these conditions the ether-insoluble form becomes in some ways more like the ether-soluble rubber. The irregularity of the melting points found for the dissolved gel crystals is consistent with a partial decomposition of very large molecules in the presence of traces of oxygen—a phenomenon over which accurate laboratory control is probably impossible. The dissolved gel seems to consist of many different kinds of molecules. Most of them may still be the same as they were before. To these it may owe its peculiar type of elasticity. It may even contain some of the same molecules as predominate in the sol portion. As contrasted with the dissolved gel, the sol form seems to have suffered no decomposition. When suitable precautions against oxidation are taken, the size of the molecules is not improbably the same as it was in the rubber tree. For this reason, the appearance of the crystals tends to be about the same every time, and the same melting point is always observed.

That the gel rubber is still very different from the sol form, even after an oxygen-fostered disaggregation permits it to dissolve in ethylbenzene or in ether, is indicated by the different elastic behavior after the rubber crystals are melted. When sol rubber melts under a liquid, each nodule quickly forms a sphere with small inclusions of the surrounding liquid.¹⁰ When the space surrounding the nodules is evacuated there form clear droplets adhering to the glass. On the other hand, when the crystals of dissolved gel rubber melt, as judged by a loss of birefringence, their original shape is held almost unchanged to a temperature of 30° C. or higher. There is slight deformation, but it is not progressive and the shape is the same 24 hours later as it is after 10 minutes. The viscosity is great and the granular structure shown in Fig. 1 (D) is preserved. This difference between the two portions is consistent with all other data¹¹—the gel has much greater stiffness and more perfect elasticity; the sol is softer, more extensible, and when deformed takes a permanent set.

By chemical action, these properties of both the sol and the gel can be changed. Thus, the crystals of dissolved gel rubber do not exhibit the more perfect elasticity after melting if they have been grown from a solution prepared by more strenuous treatment. If the gel has been dissolved by treatment with trichloroacetic acid, and crystals prepared from the solution are allowed to melt under aqueous calcium chloride solution, the clusters of crystals flow into rounded globules. This chemical action makes the gel behave more like the sol.

On the other hand, vulcanization makes the sol behave more like the gel. Sol crystals were prepared in one of the cells. The solvent was removed by washing with acetone at low temperature and all the acetone that could be siphoned was removed by that method. Always maintaining the temperature below the melting point of the crystals, a little sulfur chloride vapor was allowed to enter the cell. Much sulfur was deposited. The sulfur was dissolved with carbon disulfide at low temperature, the carbon disulfide removed with acetone, and the preparation observed with the microscope. The rubber was no longer birefringent but the original shapes of the crystalline spherulites persisted. They were pseudomorphs after the original crystals, but by combination with sulfur they had lost the molecular orientation peculiar to crystalline phases. When they were heated to 40° C. there was no further change, showing that vulcanization had increased their stiffness.

The authors have appreciated the technical advice of E. W. Washburn, the late chief of the Bureau's Chemistry Division, throughout this investigation. We are indebted to H. L. Fisher of the U. S. Rubber Company and L. G. Polhamus of the U. S. Department of Agriculture, who supplied the latex used in this investigation.

References

¹ *Bur. Standards J. Research*, **10**, 479 (1933). In the earlier paper the portions into which rubber is separated by ethyl ether were called the ether-soluble and the ether-insoluble fractions. To conform to common usage, the fractions will also be called sol and gel, and these terms refer specifically to fractions which have been purified and separated as described in the earlier paper. The use of these terms does not imply that the sol does not dissolve to form a true solution at the temperature and concentration which prevail during crystallization. They are used as names and do not necessarily refer to the sol and gel states of matter as defined by colloid chemistry.

² *Ber.*, **60B**, 1583(1928).

³ *India Rubber J.*, **60**, 1161 (1920).

⁴ *Bur. Standards J. Research*, **10**, 492 (1933); RP544.

⁵ Reference 1, p. 484-485.

⁶ Smith prepared all of the solutions and most of the crystals whose properties are reported in this section.

⁷ See figure 4, reference 1.

⁸ The number of melting point determinations is too great and the significance of the variations too doubtful to justify including at this place a chronicle of them all.

⁹ See p. 216.

¹⁰ It must be remembered that the power of surface forces to cause deformation is much greater with substances on a microscopic scale.

¹¹ Smith and Holt, *Bur. Standards J. Research*, **13**, 465 (1934).

The Influence of Catalysts in the Reaction of Sulfur on Unsaturated Organic Substances

I. A Study of Vulcanization at Elevated Temperature

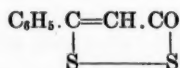
Otto Schwarzkopf

LABORATOIRE DE CHIMIE GÉNÉRALE DE LA FACULTÉ DES SCIENCES DE PARIS (SORBONNE)

1. The Object of the Investigation

The reactions of sulfur and unsaturated organic substances have not been studied very extensively up to the present time. The first work on this subject was done by Michael,¹ who studied the reactions both of styrene and of various unsaturated esters, such as those of fumaric acid, of acetylene-dicarboxylic acids, and of crotonic acid. In all these cases, it was found that between 180° and 210° C. the sulfur attaches itself to the double bond if the reaction is prolonged over a period of time varying from 10 to 40 hours.

At almost the same time Baumann and Fromm² studied the reaction of cinnamic acid³ and its esters upon sulfur. From 220° to 240° C. sulfur reacts with cinnamic ethylate by saponifying the alcohol, and by forming a compound which has the structure:



This formula was confirmed by analysis, by the determination of the molecular weight and by characteristic reactions with an alkali or phenylhydrazine. Under these conditions it acts as an internal disulfide in which one atom of sulfur is substituted for hydrogen without any change in the double bond.

The action of sulfur on ethylenic compounds has furthermore been studied in the case of certain terpenes,⁴ stilbene,⁵ indene,⁶ olefins,⁶ and naphthenes.⁶ In none of these cases have the results of the reactions been definitely ascertained.

The investigations of Meyer and Sandmeyer⁷ and of Peel and Robinson⁸ on the formation of thiophene from acetylene and sulfur should also be mentioned.

The essential character of all these reactions, which have to do with substitution or addition, is that in order to be complete they must be carried out at rather high temperatures (around 200° C.) and that they are very slow, i. e., the sulfur must act for several days under high pressure.

These reactions should then be compared with the reaction of sulfur and rubber. This reaction, which is known under the name of vulcanization, should be, from what is known today,⁹ a fixation of sulfur on the unsaturated hydrocarbon. It is surprising therefore to find in this case that the addition of sulfur is easily carried out at temperatures much below 200° C., e. g., from 80° to 130° C., and at a considerably greater rate, in fact in a few minutes.

With the aim in view of formulating a theory of vulcanization, it seemed necessary to me to seek an explanation of the differences between the vulcanization of

rubber and all the other reactions involving the fixation of sulfur on unsaturated compounds.

It might be supposed that, in the case of rubber, the action of sulfur is catalyzed by the presence of foreign substances, either those added for this purpose or those which are present in the natural rubber. These catalysts would form intermediate addition compounds which, by decomposing, would liberate active sulfur. The sulfuration of rubber would in this case proceed at a lower temperature and at a higher rate.

If this hypothesis is correct, it is evident that every reaction of sulfur with unsaturated substances should be catalyzed by catalysts of vulcanization.

Accordingly we have endeavored to find the effect of catalysts of vulcanization on all the reactions between sulfur and organic compounds.

2. Description of the Experiments

The investigation was commenced with a study of the esters of cinnamic acid, with particular attention to ethyl cinnamate. These compounds, which were used as starting points, are well known, and the products obtained by sulfuration were identified by Baumann and Fromm. Among the great number of catalysts used for vulcanization there were selected for the experiments two well defined catalysts with very different catalytic powers:

1. Hexamethylenetetramine, with relatively weak catalytic power.
2. Potassium xanthate with very great catalytic power.

According to experience in the rubber industry, the activity of these compounds can be modified by the addition of zinc oxide.

The experiments were carried out at a temperature of 160° to 170° C. where, as we shall see later, the sulfur does not react with ethyl cinnamate.

The reagents were heated on an oil bath for 9 hours at this temperature, and the reaction products were analyzed.

In the course of preliminary experiments (see Table I) we heated:

1. Sulfur with ethyl cinnamate without catalysts.
2. Sulfur with potassium xanthate.
3. Sulfur with hexamethylenetetramine.
4. Ethyl cinnamate with potassium xanthate.
5. Ethyl cinnamate with hexamethylenetetramine.

In Experiments 1 to 3, the products of the reaction were extracted with acetone, in which the cinnamate, as well as the xanthate and hexamethylenetetramine, is soluble, whereas sulfur is practically insoluble. The residue of the extraction was therefore made up of the excess of sulfur which had not reacted. The quantity of sulfur entering into the reaction is thus known. A slight loss of weight was found during the reaction, and this can be accounted for either by a slight evaporation of the ester, or by the formation of volatile products which escape. After redistillation of the acetone and drying in the oven at 70° C., the weight of the organic substance extracted by the solvent was determined.

Table I shows the weights obtained. In particular, Column 6 gives the weights of the residue which, except where there was any zinc oxide, are identical with the excess sulfur. When zinc oxide was used, it was also found in the residue.

TABLE I

Original Substance in G.			Zinc	Residue	Excess of Sulfur	Weight of Sulfur Entering into the Reaction	Loss of Weight during the Reaction	Extracts	
Sulfur	Cin-namate	Cata-lyst							
7.50	7.43	7.43	..	0.07	Acetone	0.07
7.50	13.76	7.49	7.49	..	0.21	13.46	13.7
7.50	...	xanth. 1.00	..	7.52	7.52	..	0.43	0.63	1.06
7.50	...	hexa. 1.00	..	5.98	5.98	1.52	1.59	1.01	2.60
7.50	...	hexa. 1.00	1.00	6.99	5.99	1.51	1.81	0.69	2.53
..	14.17	xanth. 1.00	..	1.18	0.27	Ether	14.2
..	14.41	hexa. 1.00	..	0.81	0.24	Ether	14.8

* The sum of the loss of weight and of the extract, equal to the weight of the reacting substances.

It is seen that at the temperature of the experiment (160–170° C.):

1. The sulfur did not react with ethyl cinnamate.
2. The sulfur did not react with the xanthate. The latter was partially decomposed into volatile substances. On the other hand, the xanthate was extracted by the acetone.
3. Sulfur reacted with hexamethylenetetramine to form a compound very rich in sulfur, which we have not yet identified exactly. It is composed of one gram of hexamethylenetetramine for every 1.5 grams of sulfur. In the presence of zinc oxide there was no change in the reaction; for example, the quantity of sulfur added to the hexamethylenetetramine molecule remains the same.
4. In the absence of sulfur, neither the xanthate nor the hexamethylenetetramine reacted with ethyl cinnamate. Here ether, in which the catalysts are insoluble, was used for the extraction.

These results show that in order to deal with the simplest phenomena, it is convenient to study first of all the reaction of sulfur on the unsaturated compound, with potassium xanthate as catalyst. In this way, the complication of a direct reaction between sulfur and the catalyst is avoided.

3. Study of the Reaction in the Presence of Potassium Xanthate

Table II contains the experiments carried out in the presence of the xanthate. The quantity of the catalyst and the quantity of the ester were both varied.

TABLE II

REACTION OF SULFUR WITH ETHYL CINNAMATE IN THE PRESENCE OF POTASSIUM XANTHATE AT 160–170° C.

Original Substance in G.				Sulfur				Acetone Extract	Gram Sulfur per Gram Cinnamate
Sulfur	Cin-namate	Xan-thate	Zinc Oxide	Residue	Excess	Entering into Reaction	Loss of Weight		
7.50	16.10	0.20	..	3.86	3.86	3.64	1.01	18.28	0.23
7.50	15.80	0.50	..	3.59	3.59	3.91	1.89	18.97	0.24
7.50	17.40	0.80	..	3.76	3.76	3.74	1.85	19.94	0.22
7.50	14.30	1.00	..	4.38	4.38	3.12	2.41	16.67	0.22
7.50	8.15	1.00	..	5.23	5.23	2.27	2.16	9.05	0.27
7.50	3.10	1.00	..	6.93	6.93	0.57	2.31	2.28	0.19
7.50	1.38	1.00	..	7.56	7.56	..	0.87	1.55	..
7.50	13.78	1.02	1.00	5.63	4.63	2.87	1.06	17.08	0.21

Average... 0.22

From this important fact it is evident that the ratio of the weight of the sulfur entering into the reaction to the weight of the cinnamate is a constant, and is independent of the quantity of the catalyst. This ratio corresponds to 1.2 atoms of sulfur for one molecule of ethyl cinnamate. Considering that our method is an indirect one, and consequently is not very precise, it can be assumed that the ratio is a stoichiometric one and corresponds to one atom of sulfur for each molecule of cinnamate.

4. Study of the Reaction in the Presence of Hexamethylenetetramine

A study of the catalytic action of hexamethylenetetramine was then undertaken. We have shown above that a complication was to be expected in the combination of sulfur and this catalyst. Table III gives the results of the weighings.

TABLE III
REACTION OF SULFUR WITH ETHYL CINNAMATE IN THE PRESENCE OF HEXAMETHYLENE-TETRAMINE AT A TEMPERATURE OF 160-170° C.

Original Substances				Residue	Sulfur		Loss of Weight	Acetone Extract	Grams of Sulfur per 1.5 Grams of Cinnamate
Sulfur	Cinna-mate	Hexa.	Zinc Oxide		Excess	Fixed			
7.50	14.11	0.99	..	3.20	3.20	4.30	1.20	17.17	0.20
7.50	14.67	0.99	1.01	3.96	3.96	3.54	1.36	17.45	0.17
Average...									0.18

It is evident at once that very much larger quantities of sulfur are involved in the reaction than the quantity corresponding to a simple fixation on hexamethylenetetramine. In Section II in fact we determined (see Table I) that the composition of the compound thus formed was 1.5 grams of sulfur per gram of hexamethylenetetramine.

It is reasonable to suppose that the quantity of sulfur fixed on the unsaturated ester is equal to the difference between the total fixed sulfur (see Column 7 in Table III) and the sulfur fixed on the hexamethylenetetramine (see Column 8 in Table I). These differences in the figures are the values shown in Column 10 in Table III. The average is 0.18 gram of sulfur per gram of the ester, which corresponds exactly to one atom of sulfur per molecule of the ester.

5. Conclusions

From these results it might be thought that in the presence of potassium xanthate or hexamethylenetetramine there is formed a compound of sulfur and cinnamate containing one atom of sulfur per molecule of the ester. This compound would not be identical to that found by Baumann and Fromm, which was mentioned in Section 1. It has been seen that it is formed at a higher temperature and that it contains two atoms of sulfur per molecule of the ester.

We attempted to isolate the compound containing one atom of sulfur, the existence of which we suspected. To this end, we distilled under reduced pressure (13 mm.) the product extracted with acetone. However, at 143° C. the ethyl cinnamate distilled almost quantitatively, whereas the sulfur remained in the residue from the distillation. Moreover, we observed a very intense Tyndall effect in the acetone solution.

Several reasons for these phenomena suggest themselves:

1. The compound formed is stable only in equilibrium with its components. By distillation the cinnamate is eliminated, equilibrium is destroyed, and the compound is quantitatively decomposed during distillation.

2. Upon the addition of acetone, with a view to extracting the substance, the compound is destroyed and the sulfur which is precipitated in the colloidal state is dissolved with ethyl cinnamate in the acetone. In the acetone solution, therefore, the cinnamate and colloidal sulfur are found in stoichiometric proportion. This would explain both the equivalence which was found and the colloidal aspect of the acetone solution.

3. A definite chemical compound is not formed, purely colloidal natural phenomena are involved, and the stoichiometric relations must be due purely to chance.

We shall not pay any particular attention at this time to experiments which would lead to a choice among these explanations. They will be the object of a future work. Nevertheless it seems of interest to us to note the parallelism between the vulcanization of rubber and the sulfuration of a well-defined unsaturated compound, and particularly the action of catalysts of vulcanization.

Finally another important similarity may be pointed out. In the case of vulcanized rubber, a definite compound has not been isolated. It is likewise known that sulfur, which alone is insoluble in acetone, passes over in large quantity when extractions are made with this solvent. The question has always arisen whether this is a case of phenomena of a colloidal nature or of the formation of chemical compounds.

We shall continue our work with a study directed particularly to simple cases where the starting compounds are well-known ones. Our efforts will be especially directed to the existence or non-existence of definite compounds. We have pointed out in this first article the difficulties before us. We shall then continue with studies of isoprene and methylbutadiene. It is conceivable that by the progressive polymerization of these products the complex case of rubber will finally be reached.

We wish to express our profound gratitude to Professor Urbain who has made it possible to carry out this experimentation. We also wish to thank M. Mathieu for his valuable criticism and his aid in the preparation of this paper.

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- ¹ Michael, *Ber.*, **28**, 1633 (1895).
- ² Baumann and Fromm, *Ibid.*, **30**, 110 (1897).
- ³ See also the recent publication by Lefèvre and Desgrez, *Compt. Rend.*, **198**, 1432, 1791 (1934).
- ⁴ Budnikow and Schillow, *Ber.*, **55**, 3848 (1922).
- ⁵ Szperl, *Roszniki Chemji*, **6**, 728 (1926).
- ⁶ Friedmann, *Ber.*, **49**, 50 (1916); *Petroleum*, **11**, 693, 978 (1916).
- ⁷ Meyer and Sandmeyer, *Ber.*, **16**, 2176.
- ⁸ Peel and Robinson, *J. Chem. Soc.*, **1928**, 2068.
- ⁹ Memmler, "Handbuch der Kautschukwissenschaften," Hirsal, 1930, page 296, etc.

The Restraining of Vulcanization in Rubber Manufacture

D. F. Twiss and F. A. Jones

Delayed-Action Accelerators

During the past few years, considerable advance has been made in the ordinary method of compounding technic with respect to scorching. The advances fall essentially into two well-marked divisions, *viz.*, the development of "delayed-action accelerators" and the addition of "vulcanization restrainers," "inhibitors of prevulcanization," or "antiscorch agents." With a true delayed-action accelerator vulcanization should not occur until a certain period of time has elapsed, after which rapid vulcanization takes place. The existence of this "time lag" can be explained on the basis that the reputed accelerators are inactive, but on heating are decomposed into other substances which constitute the real accelerators. Some organic accelerators give a temperature lag, and though comparatively safe from prevulcanization in processing, they vulcanize only above a certain critical temperature. Hence, when the rubber mixture is heated, vulcanization does not take place until this temperature is attained. Such accelerators are not delayed-action accelerators in the narrower sense. In all organic accelerators the activity can be associated with a particular grouping, and in the simplest form of accelerator generally with a particular hydrogen atom. Most if not all delayed-action accelerators can be regarded as chemical derivatives of known powerful accelerators in which the place of the active hydrogen atom is occupied by a more or less easily displaceable organic grouping; the delayed-action accelerator is consequently often a compound, *e. g.*, of the thio-ester or thio-ether (or even "thio-anhydride") type, which itself strictly is not a vulcanization accelerator, but is capable of undergoing decomposition (*e. g.*, "hydrolysis" or fission) with formation of one.

The accelerators of the ultra or semi-ultra type which need restraining fall almost entirely into two or three groups, *viz.*, the dithio-acids and the mercaptobenzothiazoles. The former class comprises more particularly the alkyl xanthates and the dithiocarbamates (and the corresponding thiuram sulfides) derived from various secondary aliphatic amines (including piperidine). The latter class is represented by 1-mercaptobenzothiazole itself, its substitution products, and the corresponding benzothiazyl sulfides.

One group of delayed-action accelerators comprises the esters, especially the aryl esters, of the dithio-acids; also the esters of the mercaptobenzothiazoles with various organic acids. These esters are commonly not produced by direct esterification, but by available convenient methods of metathesis or double decomposition.

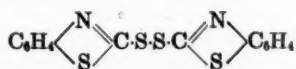
Instances of such products are 2,4-dinitrophenyl piperidinecarbothionolate, $C_6H_4(NO_2)_2-N-CS-S-C_6H_4$, and the 2,4-dinitrophenyl dialkyldithiocarbamates obtainable by the action of 1,2,4-chlorodinitrobenzene on a salt of the corresponding dithio-acid (B. P. 340,083, 340,573-4); 1-benzothiazyl thiobenzoate and

the corresponding *thiostearate*, $R-CO-S-C \begin{smallmatrix} \nearrow N \\ \searrow S \end{smallmatrix} C_6H_4$, obtainable by the action

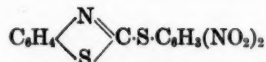
of the acyl chloride on mercaptobenzothiazole (B. P. 346,853). It is of interest that the analogous *thioacetate*, $\text{C}_6\text{H}_4\langle\text{N}\rangle\text{CS}\cdot\text{CO}\cdot\text{CH}_3$ (highly refractive prismatic needles, m. p. 86°), cannot be obtained in this way and has not previously been described in the literature; it can be easily produced by passing ketene vapors into an ethereal solution of mercaptobenzothiazole.*

As examples of the thioether or thioanhydride type may be cited the disulfides and monosulfides derived from the dithiocarbamates, such as the well-known thiuram disulfides and monosulfides $\langle\text{N}\cdot\text{CS}\cdot\text{S}_x\cdot\text{CS}\cdot\text{N}\rangle$ (cf. B. P. 177,493).

Other examples of this class which have been described are dibenzothiazyl disulfide,



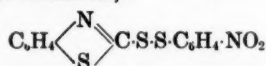
and the corresponding monosulfide (B. P. 353,580) derived from 1-mercaptobenzothiazole. The *p*-nitrophenyl disulfide, $\text{C}_6\text{H}_4\langle\text{N}\rangle\text{C}\cdot\text{S}\cdot\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, has also been described (B. P. 331,885). The 2,4-dinitrophenyl derivative of mercaptobenzothiazole



finds extensive application (B. P. 340,573-4, 340,951, etc.).

The various xanthogen disulfides (B. P. 177,493) and the monosulfides (U. S. P. 1,735,701) form another group of the thioanhydride class.

As other instances of the same class should be mentioned the alkyl and aryl thioethers of the named dithiocarbamate, benzothiazole, and xanthogen compounds, *e. g.*, the *benzyl* and *nitrobenzyl benzothiazyl sulfides*, $\text{C}_6\text{H}_4\langle\text{N}\rangle\text{C}\cdot\text{S}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\text{X}$ (B. P. 349,461), and the benzyl ester of piperidine-1-carbothionolic acid; the nitrophenyl benzothiazyl disulfides,



(B. P. 331,885), and the corresponding *o*-nitrophenyl benzothiazyl selenosulfide,

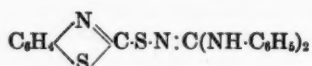
$\text{C}_6\text{H}_4\langle\text{N}\rangle\text{C}\cdot\text{S}\cdot\text{Se}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$.† Replacement of the active hydrogen of the mercaptobenzothiazoles and dithiocarbamic acids by $\cdot\text{CO}_2\text{X}$ or $\cdot\text{CH}_2\cdot\text{CO}_2\text{X}$ (where X = ethyl or $\frac{1}{2}\text{Zn}$) gives yet further members of this class of accelerator (B. P. 372,623, 353,871).

Still other versions of a restrained accelerator have been produced in the form of the formaldehyde derivative of mercaptobenzothiazole (B. P. 361,971), the formaldehyde derivative of the compound of mercaptobenzothiazole with piperidine (B. P. 377,253), the carbonyl chloride derivative of mercaptobenzothiazole (U. S. P. 1,928,773), and the cyanuryl chloride derivative of the dithiocarbamates (B. P. 378,525).

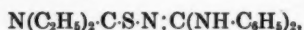
* Under similar conditions of treatment, diphenylguanidine is converted into its *triacetyl derivative*, short prisms, m. p. 122° . For these experiments, and also for the preparation of *o*-nitrophenyl benzothiazyl selenosulfide (see later), we desire to acknowledge the assistance of D. J. Hadley.

† This was prepared by the action of *o*-nitrophenyl selenobromide on mercaptobenzothiazole and also on its sodium derivative; it forms short yellow needles, m. p. about 136° .

Another group belonging to this class has been produced by the fission of the disulfide form of the accelerator with an accelerator of the amine type (B. P. 413,296), whereby molecules are obtained representing a condensed system derived from an ultra-accelerator and an amine accelerator, the constituent parts when regenerated being capable of giving the "two-accelerator effect;" *e. g.*,



comprising mercaptobenzothiazole,



comprising diethyldithiocarbamic acid, and $\text{CH}(\text{CH}_3)_2 \cdot \text{O} \cdot \text{CS} \cdot \text{S} \cdot \text{N} : \text{C}(\text{NH} \cdot \text{C}_6\text{H}_5)_2$ comprising *iso*-propylxanthic acid each coupled with diphenylguanidine. Other

examples are $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{N} \\ \diagdown \text{S} \end{array} \text{C} \cdot \text{S} \cdot \text{N}(\text{C}_2\text{H}_5)_2$, benzothiazylthiodiamylamine, obtainable from dibenzothiazyl disulfide and diamylamine; $\text{C}_4\text{H}_9\text{O} \cdot \text{CS} \cdot \text{N} : \text{C}(\text{NH} \cdot \text{C}_6\text{H}_5)_2$, thionfuroyldiphenylguanidine from dithionfuroyl disulfide and diphenylguanidine. All the known members of this group have been obtained as resinous products.

The foregoing list is typical but by no means exhaustive. Some of the above substances, *e. g.*, various disulfides and monosulfides, are on the market, frequently under more than one trade name, while others are being marketed in mixtures, *e. g.*, dinitrophenyl benzothiazyl sulfide with diphenylguanidine. In the latter case the diphenylguanidine not only assists in the "hydrolysis" or fission of the dinitrophenylbenzothiazyl sulfide, but also enhances the activity of the liberated mercaptobenzothiazole by a marked "two-accelerator" effect. It is possible indeed to get a special type of delayed-action accelerator in which the delay is due to temporary inactivation of the auxiliary activator and not of the semi-ultra-accelerator itself. As instances may be mentioned the use of diphenylguanidine tartrate (or other salt), or of triacetyldiphenylguanidine (see above) with mercaptobenzothiazole, in place of the frequent use of this accelerator with immediately free diphenylguanidine.

For fairly obvious reasons every derivative of an ultra-accelerator in which the active responsible group is weighted by a substituent will not necessarily be a good accelerator for manufacturing purposes. Manufacturing requirements in any case are so diverse that no one accelerator will satisfy all needs.

The accelerator influences not only the rate of vulcanization and the danger of prevulcanization, but also the mechanical properties of the product, such as the abrasion resistance, flexing qualities, and hysteresis behavior (including power loss, resilience, and permanent set), in addition to the aging. All applications do not call for identical qualities in these various respects, and numerous considerations weigh in the selection of an accelerator. Furthermore, the delayed action may not be of the degree desired; if too slight, the scorching danger may be still existent, and if too marked the stability of the derivative of the parent accelerator may have been rendered so great as to reduce the accelerative effect under working conditions to below a reasonable limit. The methyl iodide additive compound of dibenzothiazyl disulfide and the plain phenyl ester of piperidine-carbothionolic acid (see later) are such instances of derivatives which are too stable.

The temperature above which the "weighted" accelerator undergoes such fission is often termed its "critical temperature;" in general, the higher this temperature,

the safer the accelerator is in processing. A delayed-action accelerator so slow as to be in itself of little practical interest may in some cases be capable of giving a valuable active combination in the presence of other reagents, *e. g.*, of an accelerator of a different sort, which may not only facilitate reconversion into the accelerator proper, but may also lead with this to the development of the well-known enhanced activity known as the "two-accelerator effect." A mixture of the dinitrophenyl derivative of mercaptobenzothiazole (dinitrophenylbenzothiazyl sulfide) with diphenylguanidine is a well-known instance and is widely used.

Such mixtures indeed are often not only much quicker curing than either ingredient separately at higher temperatures, but can possess a higher critical temperature than either constituent alone, or than a simple mixture of the two unaltered parent accelerators. It is well known of course that organic bases such as diphenylguanidine increase the accelerative activity of mercaptobenzothiazole itself, but with these mixtures there is generally a marked proneness to "scorching."

The tendency of an accelerator, whether single or mixed, or even chemically modified, to cause scorching bears little relation to the actual magnitude of maintained acceleration. Thiocarbonyl, one of the earliest organic accelerators to be used, would today be regarded as relatively slow, but it has very marked tendencies to prevulcanization and scorching.

The number of patents granted in the last few years for delayed action accelerators runs into hundreds, but in general they all fall into the class of well-known ultra- or semi-ultra-accelerators in which the active group has been modified chemically, as already indicated.

A simple test (A) found useful for the comparison of the critical temperatures and degree of delayed action consists of heating a standard mixing containing the accelerator and noting the time necessary for incipient vulcanization at various temperatures. A convenient standard mixing consists of rubber 100 parts, sulfur 5 parts, zinc oxide 5 parts, accelerator 1 part. A pellet of the mixing weighing approximately 1 gram is heated under glycerol in a glass tube. This in turn is immersed in a larger glycerol bath maintained at the desired temperature. The consistency of the pellet is observed carefully by pressure with a glass rod; when incipient vulcanization occurs, the pellet becomes harder and slightly elastic. The test is conveniently made at three temperatures, 100°, 120°, and 140°.

Typical comparative results obtained are as follow:

Accelerator	Time Required for Incipient Vulcanization at		
	100°	120°	140°
Zinc <i>iso</i> -propylxanthate	4½	2½	1½
Zinc diethyldithiocarbamate	9	4½	3½
Tetramethylthiuram disulfide	31	9	3½
Tetraethylthiuram disulfide	34	10	5
Mercaptobenzothiazole	31	10	5
Diphenylguanidine	40	9	5
Hexamethylenetetramine	37	15	7½
Dinitrophenyl benzothiazyl sulfide 2 pts. + diphenylguanidine 3 pts. ("Ureka")	33	10	4
Dibenzothiazyl disulfide	>60	>40	7½
Aldehyde-ammonia	45	11	7
Crotonaldehyde-aniline	20	8	4
Piperidine piperidine-1-carbothionolate	5	3	2½
Benzothiazylthiodiamylamine	40	12	5
Thionfuroylthiodiphenylguanidine	>60	23	6
Phenyl piperidine-1-carbothionolate	17

For an accelerator of practical value, incipient vulcanization at 140° must occur in a short time because vulcanization is commonly effected near this temperature.

If "accelerators" are very slow at 140° their accelerating effect is not likely to be of practical importance. The method just described has advantages in that it is possible to compare the accelerating qualities and scorching tendencies of experimental substances of which only a small quantity is available.

The method also is rapid, and several accelerators can be tested concurrently by using separate glass tubes heated in the same bath. Reproducible results are easily obtained after a little experience. Except where otherwise stated, numerical results given in this paper were obtained by this method.

When carrying out the test at 100° it is hardly necessary to carry the heating time beyond 60 minutes, because if an accelerator gives no sign of prevulcanization in this time its "scorching behavior" may be regarded as good. To be of practical interest it must of course vulcanize satisfactorily at higher temperatures.

Other methods of estimation of scorch-retarding powers are more complicated and demand elaborate or expensive equipment.

A more exact method (B) of determining the comparative scorching tendencies of accelerators, but one which requires more of the rubber mixture, is based on the use of the plastometer. In this method standard pellets cut from the mixing are heated at a temperature approximating to the prospective processing temperatures, *e. g.*, at 105°, and at intervals the elasticity of the rubber is tested by placing a pellet between two horizontal parallel plates, the upper one of which is supported by the pellet and carries a known weight. The amount of recovery of the rubber after release of the load is recorded. By drawing a curve for the degree of recovery after various periods of heating, a curve is obtained which shows the rate of development of vulcanization for the mixture and temperature in question. Comparison of such curves reveals the relative scorching tendencies of various accelerators (cf. Dieterich and Davies, *Ind. Eng. Chem., Anal. Ed.*, 3, 297 (1931); Williams, *Ind. Eng. Chem.*, 16, 362 (1924); Krall, *ibid.*, 922).

Another method (C) which has been used for comparing the prevulcanizing tendencies of stocks consists of heating a number of pellets of the stock in an oven for definite times and then immersing them in a rubber solvent. The time of heating which is required to give a rubber sufficiently vulcanized to attain an arbitrary standard of reduced solubility, or of increased resistance to swelling by a solvent under standardized conditions, is used as the basis of comparison (Thies, *Ind. Eng. Chem.*, 23, 1357 (1931)). This method only measures incipient vulcanization or scorching at a more advanced state than the two preceding methods. The following figures give some indication of this.

A mixture of rubber 100, zinc oxide 5, sulfur 5, and accelerator 1, was heated for the minimum period sufficient for attainment of a condition indicating incipient vulcanization by methods A and C, respectively. The coefficient of vulcanization also was then determined for additional interest.

Method	Accelerator	Conditions of Heating Necessary		Coefficient of Vulcanization
A	Diphenylguanidine	110°	17 min.	0.10
C	Diphenylguanidine	110°	25 min.	0.13
A	Di- <i>o</i> -tolylguanidine	110°	12 min.	0.13
C	Di- <i>o</i> -tolylguanidine	110°	23 min.	0.19

Antiscorch Agents

In recent years another important class of materials has been developed for the prevention of prevulcanization, *viz.*, "scorch-retarders" or "antiscorching agents." These delay vulcanization at temperatures at which mixing, calendering, extruding,

etc., are carried out, but exert little influence at the vulcanization temperature proper. Such agents should be free from other complications; they should not affect the color of the mixing nor impair the aging properties of the rubber. They should be practically free from odor, and be so active that only very small amounts are required to give the desired scorch-retarding effect. They should have no adverse effect on the physical properties of the vulcanized rubber.

Because a substance may act as a scorch-retarder with one accelerator, *e. g.*, with mercaptobenzothiazole, it does not necessarily retard scorching with all classes of accelerators. For example, cadmium oxide has been claimed to be definitely a preventive against prevulcanization when used with tetramethylthiuram monosulfide (U. S. P. 1,822,561), but when used with mercaptobenzothiazole, di-*o*-tolylguanidine, and accelerators of some other classes (such as the aldehyde-amines) it is not an anti-scorch agent, and actually increases the scorching tendency in no uncertain manner.

Pine tar, rosin oil, and stearic acid (in larger proportions), which for a long time have been used to increase the plasticity of unvulcanized mixed rubber, are incidentally also antiscorch agents. Pine tar, for example, has a marked retarding action on vulcanization at 80–113°, but at 130° and above has little effect (Thies, *loc. cit.*).

Certain synthetic resins of the Bakelite type (phenolformaldehyde) also have antiscorch properties, as also have glyptal resins (B. P. 367,901; also Naunton and Siddle, *India-Rubber J.*, 82, 535 (1931)).

Unfortunately, glyptal resin also interferes with vulcanization at higher temperatures to such an extent that it is possible only to use such small quantities that the scorch-retarding effectiveness is not as great as with some of the other antiscorch agents available. In glyptal resins, the proportion of free acid in the material may vary considerably according to the conditions of preparation, and their effectiveness in restraining premature vulcanization depends almost directly on the proportion of free acid present.

Free acids themselves and their anhydrides are also effective antiscorching agents, and can be added to the rubber mixing in a variety of ways. They may, for instance, be first combined with a basic accelerator such as diphenylguanidine. They may alternatively be added directly in powdered form. Results obtained by the scorching test using pellets of rubber mixing heated in glycerol are as follows. *Mixing*: rubber 100 parts, sulfur 5 parts, zinc oxide 5 parts, mixture of dinitrophenyl benzothiazyl sulfide (2 parts) + diphenylguanidine (3 parts) 1 part, acidic antiscorch agent 1 part.

Acid Used	Minutes Required for Incipient Vulcanization at		
	100°	120°	140°
Citric	>60	48	10
Tartaric	55	24	8
Lactic	58	27	10
Succinic	55	15	8
Oxalic	58	29	11
Sebacic	45	21	7
Adipic	50	26	7
None	35	11	6

On account of their sparing solubility in rubber, the above acids when added in powdered form are difficult to incorporate uniformly. Phthalic anhydride, which has been marketed commercially as a vulcanization restrainer, also shows this disadvantage.

Benzoic acid dissolves in rubber much more readily. A mixture of this acid

with zinc oxide has also been marketed as an antiscorch agent (under a proprietary name). Unfortunately, marked solubility in rubber, though facilitating uniform dispersion, often gives rise also to the serious disadvantage of "blooming" on the surface of the vulcanized rubber, *e. g.*, during stocking.

If, however, some of the above acids which are not dissolved by the rubber are combined with a basic substance such as aniline, a much better dispersion can be effected, and at the same time the antiscorch properties of the acids themselves are still observable.

Scorching tests using an arylamine for this purpose are as follows. *Mixing:* rubber 100, sulfur 5, zinc oxide 5, mixture of dinitrophenyl benzothiazyl sulfide (2 parts) + diphenylguanidine (3 parts) 1, antiscorch substance 1.

Antiscorch Agent	Minutes Required for Incipient Vulcanization		
	100°	120°	140°
Aniline acid tartrate	58	26	10
Aniline diacid citrate	>60	25	11
Aniline acid citrate	>60	30	12
<i>o</i> -Toluidine acid citrate	58	27	9
<i>p</i> -Toluidine acid citrate	>60	33	8
<i>p</i> -Toluidine diacid citrate	55	26	10
Aniline acid sulfate	58	17	9½
Aniline diacid phosphate	54	17	9
None	35	11	6

Alternatively, the acid may be incorporated in the rubber in combination with a basic accelerator such as diphenylguanidine, forming again a delayed-action accelerator. "Delayed-action" accelerators comprising a powerful accelerator such as mercaptobenzothiazole and a salt of diphenylguanidine, *e. g.*, with an organic acid, are on the market under trade names.

Accelerator	Minutes Required for Incipient Vulcanisation		
	100°	120°	140°
Diphenylguanidine 0.6 part	25	9	5
Dinitrophenyl benzothiazyl sulfide 0.4 part			
Diphenylguanidine hydrogen oxalate 0.9 part	40	12	7
Dinitrophenyl benzothiazyl sulfide 0.4 part			

It will be seen, however, that in all the preceding examples the use of such acid substances gives a certain amount of retardation of vulcanization even at 140°. This is undesirable because the rubber is required to vulcanize at a normal rate at proper curing temperatures. In order to reduce or eliminate this undesirable feature, use may be made of acids which undergo decomposition when they are heated to vulcanizing temperatures, giving products which are neutral or less acid. Malonic acid lends itself to such application (as do most other acids containing the grouping $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CO}\cdot$ or $\text{CO}_2\text{H}\cdot\text{CO}\cdot$) and may be used as a scorch-preventing agent, either alone or combined with a basic substance such as aniline or with a basic accelerator, *e. g.*, diphenylguanidine. At vulcanizing temperatures malonic acid decomposes, with formation of a semimolecular proportion of the much weaker acetic acid, so that at the higher temperatures the restraining effect of the malonic acid disappears by chemical decomposition as well as by concurrent neutralization to some extent by basic components of the rubber mixture. Thus:

Restraining Agent (1%)	Minutes Required for Incipient Vulcanisation		
	100°	120°	140°
Blank mix (p. 234)	25	9	5
Malonic acid	>60	27	8
Citric acid	>60	48	10
Lactic acid	58	27	10
Diphenylguanidine malonate	33	10	5
Diphenylguanidine acid malonate	35	11	5

As decomposition of the malonic acid gives rise to another acid, though weaker and in semi-equivalent proportion, vulcanization at 140° still tends to be a little slower than it would be without the antiscorching acid. Substances are known, however, which will further activate accelerators. For example, in the vulcanization of rubber goods in heated air, the effect of an accelerator of vulcanization, which in these circumstances is essential, can be increased by using an atmosphere containing ammonia. Organic bases such as piperidine can be incorporated in an accelerated rubber mixing for a similar purpose. This possibility can be extended to render vulcanization restrainers still more definite in their action. Urea itself does not affect the rate of vulcanization, but at higher vulcanizing temperatures it decomposes to give ammonia. Urea itself consequently does not affect processing. If urea is added to a mixture containing a vulcanization restrainer of acidic type, the latter exerts its characteristic effect substantially unimpaired by the urea. When, however, the mixture is heated to a full vulcanizing temperature, the urea decomposes, yielding ammonia, which neutralizes any residual restraining agent and further activates any organic accelerator, thereby doubly ensuring effective and rapid vulcanization in the desired temperature range. As the acidic restrainer may itself be of the class just described, which independently undergoes decomposition with substantial decrease in its acidity, it is possible to superpose the advantages from both these sources. Thiourea has a similar action. This combination of effects is illustrated in the following tests:

Restraining Agent	Minutes Required for Incipient Vulcanisation		
	100°	120°	140°
Blank (p. 234)	26	10	6
1% Urea acid tartrate	35	11	5½
1% Urea malonate	27	8	5
1% Urea acid malonate	35	17	6
1% Urea acid succinate	45	15	6
1% Thiourea acid oxalate	55	20	6½
1% Urea acid sulfate	50	14	7½

These results reveal the advantage derivable from the use of such a chemical device for restraining vulcanization at the lower temperatures, such as are likely to be encountered during the processing operations which are necessary before vulcanization is desired. They also indicate, however, that the success in solving this problem is still only partial, and that a method of compounding with effectual prevention of any premature action by an ultra-accelerator at 100°, while permitting it to act without restraint in the neighborhood of 140°, has still to be discovered.

The present-day demand for shorter and shorter periods of vulcanization is a natural one in view of the need to apply expensive equipment to the greatest possible output with the smallest over-all cost. Moreover the rapid production of articles by the use of modern synthetic moulding powders has made present-day methods of manufacture of rubber articles by vulcanization appear painfully time-consuming. The need for a method of acceleration which will not be operative

at processing temperature, and yet will be very active a few degrees higher, is a real one; whether or not this need will be first met with an accelerator with an ideal "trigger" action or by an ideal restrainer, or by some combination of these or some new principle, the result when attained will be of great importance. The difficulty of the problem is increased, however, by the constant need to bear cognizance of other correlated effects, particularly on the various physical and mechanical properties of the vulcanized products. It must be borne in mind, moreover, that the above requirements are more or less peculiar to the manufacture of rubber by "dry" methods, and even here occasionally "scorching" accelerators may be demanded for special purposes. In latex technic the need for a "delayed-action" accelerator is rarely likely to be encountered seriously.

The Influence of Certain Colored Substances on the Autooxidation of Balata and of Rubber

H. F. Bondy

LABORATOIRE DE CHIMIE ORGANIQUE, COLLÈGE DE FRANCE, PARIS

THEORETICAL PART

A. Introduction

Thanks to the numerous investigations of Moureu and Dufraisse,¹ a large number of substances are now known which retard the autooxidation of oxidizable substances. These retarding substances were given the name of antioxygens by the authors. Dufraisse and his collaborators² have studied, with special attention to rubber, a certain number of antioxygens which greatly retard autooxidation and the changes which take place during aging.

In a preceding work³ I showed, by a study of different portions of the acetone extract of rubber, that certain substances exercise an antioxygenic effect which is the greater the more highly colored they are. The question then arose whether, in addition to antioxygens which act chemically, there may not be colored substances capable of retarding the autooxidation of rubber by physical means by absorbing active luminous radiation. I thus ignored completely spontaneous autooxidation, which is quite a different phenomenon from the one I did investigate. In the work referred to above, some experiments on colored substances were described which showed, for example, that azobenzene and α -benzeneazo- β -naphthylamine had a very great antioxygenic action, whereas alizarin and carotene were almost inactive.

The present work will show whether colored substances are capable, by purely physical means, of preventing the autooxidation of rubber and of substances allied to rubber, such as balata and gutta-percha.⁴

B. Technique

1. *Determination of the Degree of Autooxidation of Rubber and of Balata by Means of Viscosity Measurements.*—In order to determine the degree of autooxidation of rubber and of balata, the viscosities of solutions with a rubber content corresponding to 0.2 of a molecule of isoprene in tetralin were measured. This method was based upon the numerous works of Staudinger,⁵ according to which large molecules give very viscous solutions, whereas small molecules give solutions of low viscosity. When autooxidation takes place, the oxygen becomes fixed in the peroxide form. The peroxides formed are not stable, and the large molecules decompose into smaller molecules, and the viscosity diminishes. Measurements of viscosity thus offer an excellent means of determining the autooxidizability of these highly polymerized substances.

The measurements were made in a Ubbelodhe viscosimeter.

The tables which follow give the values of the relative viscosity μ_r measured at two different pressures, viz., 70 and 20 cm. of mercury. Since very large molecules are concerned, the viscosity at 70 cm. is always a little lower than at 20 cm. The relative viscosity μ_r is equal to the product of the pressure P_1 and the time of flow t_1 of the solution, divided by the product of pressure P_2 and the rate of flow of the pure solvent t_2 :

$$\mu_r = \frac{P_{1t_1}}{P_{2t_2}}$$

2. *Mode of Operation.*—Autooxidation was induced by irradiation of the solid rubber or balata in air.

In order to measure the effect produced, two 0.2 molecular solutions of the solid substances in tetralin, before and after irradiation, were prepared. Measurements of their viscosity show the degree of degradation brought about by autooxidation.

Daylight was used as the source of light. However, since it was difficult to obtain comparable tests with daylight because of variations in the intensity of the light, ultra-violet light was also employed. In addition to its uniformity, ultra-violet light offered the advantage of giving much more rapid results. The results from the two sources are moreover identical, although the ozone which is formed during ultra-violet irradiation might be expected to enter into the reaction.

For these tests balata was the chief material used, because it is much easier to obtain in the pure state and is much easier to handle than is rubber. It is as sensitive to oxygen as is the latter, and is influenced by the same antioxygens. All the tests with balata can be easily reproduced in an identical way and are applicable directly to rubber.

C. Results Obtained by Incorporating in Solid Balata the Substances under Investigation

1. *Action of Some Colored Hydrocarbons.*—In Table I are summarized the results which were obtained when colored hydrocarbons were incorporated in solid balata. Rubrene and bidiphenyleneethylene are red hydrocarbons; dehydrorubrene⁶ is colorless with a violet fluorescence. At times the irradiation brought about the transformation of part of the balata into an insoluble substance. The percentage of insoluble substance is shown in the column next to the viscosity.

TABLE I
HYDROCARBONS. TWO-TENTH MOLECULAR SOLUTIONS IN TETRALIN

	Purified Balata			Balata + 5% Rubrene			Balata + 5% Dehydrorubrene			Balata + 5% Bidiphenyleneethylene		
	70 Cm.	20 Cm.	Per cent Insol-uble	70 Cm.	20 Cm.	Per cent Insol-uble	70 Cm.	20 Cm.	Per cent Insol-uble	70 Cm.	20 Cm.	Per cent Insol-uble
Not irradiated	7.4	7.7	0	7.4	7.6	0	7.5	7.7	0	7.2	7.6	0
Irradiated:												
4 hours ultra-violet	5.3	5.5	0	5.2	5.3	0	4.8	4.9	0	6.9	7.1	0
8 hours ultra-violet	3.8	3.9	1.2	3.7	3.8	2.3	4.1	4.2	1.6	6.6	6.9	0
4 days daylight	5.4	5.6	0	5.2	5.3	1.7	5.2	5.4	0	6.9	7.2	0
11 days daylight	2.2	2.2	2.6	3.3	3.3	5.1	3.0	3.0	1.7	6.2	6.3	0
In solution:												
1 day daylight	5.9	6.1	0	1.7	1.7	0	2.2	2.2	0	6.2	6.3	0
2 days daylight	4.3	4.3	0	1.6	1.6	0	1.9	1.9	0	4.1	4.2	0
Iodine liberated:												
After 11 days daylight	positive			positive			positive			negative		
Appearance after 11 days daylight	very friable			friable			friable			unchanged		

Table I shows that rubrene and dehydrorubrene have almost no effect upon the autooxidation of solid balata. In spite of their presence, a peroxidation takes place, which can be detected by one of the characteristic reactions of peroxides.

TABLE II
QUINONES. TWO-TENTHS MOLECULAR SOLUTIONS IN TETRALIN

	Purified Balata	Balata + 5% of Anthraquinone	Balata + 5% of Acenaphthene- quinone	Balata + 5% of Para- quinone	Balata + 5% of Phenanthrenequinone	Balata + 5% of α -Naphtho- quinone	Balata + 5% of β -Naphtho- quinone
	Per cent 70 20 Insol- Cm. Cm. uible	Per cent 70 20 Insol- Cm. Cm. uible	Per cent 70 20 Insol- Cm. Cm. uible	Per cent 70 20 Insol- Cm. Cm. uible	Per cent 70 20 Insol- Cm. Cm. uible	Per cent 70 20 Insol- Cm. Cm. uible	Per cent 70 20 Insol- Cm. Cm. uible
Not irradiated	7.4 7.7 0	6.9 6.9 0	7.2 7.2 0	7.8 8.2 0	7.3 7.5 0	7.4 7.7 0	7.5 7.9 0
4 hours ultra-violet	5.3 5.6 0	3.3 3.3 0	5.0 5.0 0	6.0 6.4 traces	5.7 5.9 4.5	6.8 7.1 8.7	7.5 7.9 traces
8 hours ultra-violet	3.8 3.9 1.2	2.2 2.2 traces	3.3 3.3 0	4.7 4.8 2.3	4.8 4.9 8.8	6.0 6.3 16.3	7.5 8.0 traces
4 days daylight	5.4 5.6 0	4.0 3.9 0	6.4 6.3 0	5.1 5.3 traces	3.9 4.1 11.6	5.1 5.4 31.4	7.7 8.1 traces
11 days daylight	2.2 2.2 2.6	2.7 2.8 0	4.8 4.7 0	2.9 2.9 2.2	3.8 4.0 11.1	3.3 3.6 41.2	7.2 7.6 traces
In solution:							
1 day daylight	5.9 6.1 0	2.9 2.9 0
2 days daylight	4.3 4.4 0	2.9 2.9 0	4.3 4.3 0	4.3 4.3 0	3.9 3.9 0	4.2 4.2 0	4.6 4.7 0
Iodine liberated after 11 days daylight	positive	positive	slightly positive	positive	slightly positive	negative	negative
Appearance after 11 days daylight	very friable	very friable	slightly friable	friable	friable	unaltered	unaltered

If in fact, mixtures of balata and rubrene or dehydrorubrene are treated after an irradiation of eleven days with potassium iodide, sulfuric acid and starch, the iodine is liberated. This autooxidation is very marked, as is shown by the external appearance of the mixtures, which become very friable. With dissolved balata the results are different. By exposure to air and to light of solutions of balata in the presence of rubrene and dehydrorubrene, it was proved that the viscosity becomes much smaller than the viscosity of pure balata. In this case the two hydrocarbons exerted a distinctly proöxygenic action. This fact has already been proved by Gaffron⁷ in the case of rubrene.

Bidiphenyleneethylene on the other hand is a rather active antioxygen when it is incorporated in solid balata; whereas when added to balata in solution it is without action.

I have often observed that substances which have an antioxygenic effect on solid substances become ineffective in solution, for example, the acetone extract of rubber. Perhaps the concentration of the antioxygen which is used becomes too weak in solution. The solid mixture of balata and bidiphenyleneethylene did not liberate iodine of potassium iodide, even after eleven days of irradiation. Its outward appearance was unchanged, and it resembled in all ways balata which had not been irradiated.

2. *Action of Quinones.*—Table II gives the results of incorporating quinones in balata.

Anthraquinone had a highly proöxygenic effect on solid balata. In the case of dissolved balata, it induced such an intense autooxidation that changes in the viscosity could be observed during the very short time required for a measurement.

Acenaphthenequinone was likewise a proöxygen for dissolved balata; but it was almost without effect on solid balata.

Paraquinone did not have any special effect.

Phenanthrenequinone had a highly polymerizing action which was manifest in an increase in the quantity of insoluble substance during irradiation.

α -Naphthoquinone showed this polymerizing action to an even greater extent; the quantity of insoluble substance increased greatly with the time of irradiation. Pummerer⁸ too had already found this effect for a certain number of substances. At the same time α -naphthoquinone seemed to have a certain antioxygenic action, although it was not easy to verify this fact by measurements of the viscosity, because of the fact that part of the substance became insoluble. However the negative reaction of iodine and the external appearance of the product, which remained unchanged, make this supposition possible.

β -Naphthoquinone was a distinct antioxygen, and contrary to the behavior of α -naphthoquinone, it had no polymerizing action.

In these experiments only one per cent of α -naphthoquinone was incorporated in the balata, whereas 5 per cent was used in the experiments in Table II. The quantity of insoluble substance formed was the same in both cases. Its formation was therefore due to a catalytic reaction, independent of the quantity of the catalyst. It increased when the irradiation was carried out in an atmosphere of nitrogen. When the mixture was stored in an atmosphere of nitrogen but in darkness, there was no polymerization. The catalytic reaction was therefore caused by luminous irradiation, even in the absence of oxygen. In order to explain this it may be imagined that under the influence of α -naphthoquinone and of light, the macromolecules of balata react upon each other by opening of their double bonds to give 3-dimensional insoluble molecules.⁹

In column 3 of Table III 5 per cent of α -naphthoquinone was added to the balata and also 5 per cent of aldol- α -naphthylamine. This latter compound slightly reduced the polymerizing properties of α -naphthoquinone, but did not suppress them completely.

TABLE III
RELATIVE VISCOSITIES OF 0.2 MOLECULAR SOLUTIONS IN TETRALIN

	Purified Balata			Balata + 1% of α -Naphthoquinone			Balata + 5% of α -Naphthoquinone + 5% of Aldol- α -Naphthylamine			Balata + 5% Aldol- α -Naphthylamine		
	Per cent			Per cent			Per cent			Per cent		
	70 Cm.	20 Cm.	Insol-uble	70 Cm.	20 Cm.	Insol-uble	70 Cm.	20 Cm.	Insol-uble	70 Cm.	20 Cm.	Insol-uble
Not irradiated	7.1	7.4	0	7.1	7.4	0	7.0	7.3	0	7.1	7.4	0
8 hours ultra-violet	3.6	3.7	1.2	5.5	5.7	15.8	6.3	6.4	5.6	6.5	6.7	2.4
4 days daylight	4.2	4.3	0	4.8	5.0	30.0	5.4	5.7	14.5	5.9	6.1	2.3
4 days daylight in nitrogen	7.2	7.4	0	4.4	4.7	48.4	5.8	6.0	13.0	6.7	7.0	6.3

Column 4 shows that aldol- α -naphthylamine likewise possesses weakly polymerizing properties.

In the acetone extract of rubber there must likewise be substances which possess polymerizing properties. In fact, when a rubber solution was prepared in an atmosphere of nitrogen and a little acetone extract was added, the viscosity immediately began to increase, and after three weeks the solution was completely jellified. When air was then introduced, the gel was transformed after a short time into a solution of low viscosity. This shows that, in an atmosphere of nitrogen, certain substances contained in the acetone extract of rubber induce the formation of 3-dimensional molecules, whereas in the presence of air and in solution the oxygen cleavage becomes predominant.

D. Results Obtained by Filtering the Light¹⁰

If the experiments described up to now are considered, it is seen that the two most highly colored substances, bidiphenyleneethylene and β -naphthoquinone are at the same time the ones which have the greatest antioxygenic action. However, it was difficult in mixing rubber and protective substances to prove that it was light absorption alone that brought about the antioxygenic effect, since in this case it was impossible to eliminate the chemical effect.

In the experiments which follow, the light was first passed through solutions of colored substances, and the purified, solid balata was irradiated in contact with air with this filtered light.

Table IV shows that purified balata irradiated by light passed through toluene was very strongly autooxidized. Under these conditions, the balata behaved exactly as if the luminous rays had impinged upon it directly.

When on the contrary the light was first filtered through one per cent toluene solutions of colored substances, which had been found to be active after having been mixed with solid balata, there was no longer any autooxidation whatsoever. The viscosities remained absolutely constant. This proves that the autooxidation of balata can be prevented by certain colored substances which absorb active radiations. It cannot here be a case of chemical action, since the colored substances were not in contact with the balata.

It was also proved that these substances possess a definite protective influence when the light is first passed through their solutions. One may therefore ask why they have only such a feeble action when they are mixed directly into balata. Perhaps the following is the explanation. If a colored substance, mixed with solid balata, owes its antioxygenic action to its absorption of luminous radiation, it must be assumed that the colored substance surrounds each molecule, as it were, and thus protects it against luminous radiation. In this case it is necessary for the mixture produced to be very intimate, *i. e.*, the colored substances must be dissolved in the balata.

It follows that the substances shown in Table IV must be very easily soluble in balata, and that those in Table V are difficultly soluble. This can easily be verified with alizarin and phenanthrenequinone, for example, which are difficultly soluble in hydrocarbons. As for α -naphthoquinone, which is very soluble in the latter, it is not known exactly whether this substance has highly antioxygenic properties, because during the irradiation of the solid mixture it is the polymerizing action which is most strongly manifest.

TABLE IV
RELATIVE VISCOSITIES OF 0.2 MOLECULAR SOLUTIONS IN TETRALIN

	Purified Balata Behind		Balata Behind 1% Asobenzene in		Balata Behind 1% α -Benzene- β -Naphthylamine in		Balata Behind 1% Bidiphenyl-eneethylene in		Balata Behind 1% β -Naphthoquinone in	
	Toluene		Toluene		Toluene		Toluene		Toluene	
	70 Cm.	20 Cm.	70 Cm.	20 Cm.	70 Cm.	20 Cm.	70 Cm.	20 Cm.	70 Cm.	20 Cm.
Not irradiated	7.1	7.4	7.1	7.4	7.1	7.4	7.1	7.4	7.1	7.4
4 hours ultra-violet	5.5	5.7	7.2	7.5	7.1	7.4	7.1	7.3	7.3	7.5
8 hours ultra-violet	3.1	3.2	7.2	7.5	7.2	7.5	7.2	7.5	7.2	7.4
4 days daylight	4.2	4.3	7.1	7.4	7.0	7.3	7.2	7.4	7.2	7.4
10 days daylight	1.9	1.9	7.1	7.4	7.0	7.3	7.1	7.3	7.2	7.4

TABLE V
RELATIVE VISCOSITIES OF 0.2 MOLECULAR SOLUTIONS IN TETRALIN

	Purified Balata in		Balata Behind Alizarin in		Balata Behind Phenanthrene-quinone in		Balata Behind α -Naphthoquinone in	
	Toluene		Toluene		Toluene		Toluene	
	70 Cm.	20 Cm.	70 Cm.	20 Cm.	70 Cm.	20 Cm.	70 Cm.	20 Cm.
Not irradiated	7.1	7.4	7.1	7.4	7.1	7.4	7.1	7.4
4 hours ultra-violet	5.5	5.7	7.0	7.2	7.0	7.2	7.2	7.5
8 hours ultra-violet	3.1	3.2	6.9	7.0	7.2	7.5	7.0	7.3
4 days daylight	4.2	4.3	6.5	6.7	7.0	7.3	7.0	7.2
10 days daylight	2.1	2.1	5.5	5.6	6.4	6.6	6.8	7.0

A colored substance which absorbs active radiations of light can therefore inhibit autooxidation only if it is easily soluble in balata or in rubber.

3. *Balata Irradiated through Solutions of the Acetone Extract of Rubber.*—In the experiments which follow, the attempt was made to determine whether the antioxygenic action of the acetone extract of rubber was not due in part to the brown coloring substances which it contained.

To this end, toluene solutions of the total extract obtained by extraction of crude rubber with acetone were used at concentrations of 1, 0.5, and 0.1 per cent. The light passed through these solutions before reaching the balata.

Table VI shows clearly that, even at a concentration of 0.1 per cent, the extract is still active. I do not wish to conclude from this that the natural protective agents in rubber are only colored substances. On the contrary, it is very probable that there are still other antioxidants besides the colored substances. However, it is certain that a large part of the effect due to natural substances formed by the plant must be attributed to colored substances.

TABLE VI
RELATIVE VISCOSITIES OF 0.2 MOLECULAR SOLUTIONS IN TETRALIN

	Purified Balata Behind Toluene		Balata Behind 1% Rubber Extract in Toluene		Balata Behind 0.5% Rubber Extract in Toluene		Balata Behind 0.1% Rubber Extract in Toluene	
	70 Cm.	20 Cm.	70 Cm.	20 Cm.	70 Cm.	20 Cm.	70 Cm.	20 Cm.
Not irradiated	7.1	7.4	7.1	7.4	7.1	7.4	7.1	7.4
4 hours ultra-violet	5.5	5.7	7.0	7.4	7.0	7.2	5.9	6.1
8 hours ultra-violet	3.1	3.2	7.2	7.4	5.8	6.0	2.7	2.7
4 days daylight	2.6	2.6	6.2	6.4	5.7	5.9	3.0	3.0
10 days daylight	2.1	2.1	5.8	6.1	4.9	5.0	2.5	2.5

Bruson¹¹ also isolated dark brown oils from the acetone extract of rubber. In an earlier work³ I isolated basic substances which were colored dark brown and were extremely active. At least part of the effect of these substances must therefore be attributed to their color.

4. *Rubber Irradiated through Solutions of Colored Substances and of the Acetone Extract.*—Experiments comparable to those with balata which have just been described were also carried out with rubber. The rubber used for this purpose was first extracted with acetone to remove its natural antioxidants.

Table VII shows clearly that the results with balata are directly applicable to rubber, in fact the results are the same. Consequently if light is passed through solutions of certain colored substances or through solutions of the acetone extract of rubber, the light no longer contains radiations which are capable of inducing the autooxidation of rubber.

TABLE VII
RELATIVE VISCOSITIES OF 0.2 MOLECULAR SOLUTIONS IN TETRALIN

	Rubber Extracted with Acetone in Toluene		Rubber Behind 1% of Azoben- zene in Toluene		Rubber Behind 1% of Ben- zene azo- β - Naphthyl- amine		Rubber Behind 1% of Bidi- phenylene- ethylene		Rubber Behind 1% of β - Naphtho- quinone		Rubber Behind 1% Rubber Extract		Rubber Behind 0.5% Rubber Extract	
	70 Cm.	20 Cm.	70 Cm.	20 Cm.	70 Cm.	20 Cm.	70 Cm.	20 Cm.	70 Cm.	20 Cm.	70 Cm.	20 Cm.	70 Cm.	20 Cm.
Not irradiated	11.5	14.7	11.5	14.7	11.5	14.7	11.5	14.7	11.5	14.7	11.5	14.7	11.5	14.7
8 hours ultra-violet	6.1	7.4	11.2	14.0	10.5	13.3	9.7	11.9	10.1	12.4	10.6	12.4	9.9	12.1
10 days daylight	2.0	2.0	11.4	14.2	10.9	13.4	9.9	11.9	10.2	12.5	9.7	11.7	4.1	4.3

5. *Balata Irradiated through Solutions Which Allow Only Radiations of a Definite Wave Length to Pass.*—After having shown in the preceding experiments that certain colored substances have an inhibitory action on the autooxidation of rubber

and of balata by absorbing active radiations, it was of interest to know which radiations were particularly active in inducing this autooxidation. It was accordingly necessary to determine in which region of the spectrum a colored substance must absorb light in order for it to have an inhibitory action upon autooxidation.

TABLE VIII
RELATIVE VISCOSITIES OF 0.2 MOLECULAR SOLUTIONS IN TETRALIN

	Purified Balata Behind Water		Balata Behind Potassium Chromate		Balata Behind Copper Sulfate		Balata Behind Crystallized Violet		Balata Behind Quinine Sulfate	
	70 Cm.	20 Cm.	70 Cm.	20 Cm.	70 Cm.	20 Cm.	70 Cm.	20 Cm.	70 Cm.	20 Cm.
Not irradiated	7.1	7.4	7.1	7.4	7.1	7.4	7.1	7.4	7.1	7.4
4 days daylight	3.3	3.4	6.4	6.6	3.0	3.0	3.2	3.3	4.9	5.0
10 days daylight	2.0	2.0	6.1	6.3	2.0	2.0	2.0	2.0	3.5	3.6

To this end light was passed through certain colored solutions which absorb a sharply defined wave length. When the balata was placed behind a screen of water, marked autooxidation resulted. This may be explained by the fact that the water allowed almost all the radiations to pass and absorbed only the smallest ultra-violet radiations beyond 200μ . When the light was passed through potassium chromate, a large part of the active radiation was absorbed. The absorption was however not complete, since there was still a slight degradation by oxygen. The potassium chromate absorbed all light of a short wave length beyond 450μ , and so there remained active radiations of length greater than 450μ , although they were only in small proportion and had little energy.

When the light was passed through a solution of copper sulfate, total degradation of the balata occurred. Therefore the copper sulfate did not absorb any active radiations. Since it absorbed all long-wave light beyond 525μ , there were no active radiations within this region.

With a solution of crystal violet, complete degradation likewise resulted. Since crystal violet absorbed all long-wave light up to approximately 480μ , there were no longer active radiations in this region.

Quinine sulfate absorbed all light of wave lengths below 400μ . As might be supposed, it is obvious that this region contains active radiations, since the balata was degraded in that region. However, it was less degraded than behind a screen of water.

6. *Rubber Irradiated through Solutions Which Allow Radiations of Only Definite Wave Length to Pass.*—In Table IX are given the results of experiments on rubber which are similar to those on balata.

TABLE IX
RELATIVE VISCOSITIES OF 0.2 MOLECULAR SOLUTIONS IN TETRALIN

	Rubber Extracted from Ace- tone Behind Water		Rubber Behind Potassium Chromate		Rubber Behind Copper Sulfate		Balata Behind Crystal Violet		Balata Behind Quinine Sulfate	
	70 Cm.	20 Cm.	70 Cm.	20 Cm.	70 Cm.	20 Cm.	70 Cm.	20 Cm.	70 Cm.	20 Cm.
Not irradiated	11.5	14.7	11.5	14.7	11.5	14.7	11.5	14.7	11.5	14.7
10 days daylight	2.0	2.0	10.5	12.8	2.2	2.2	2.1	2.1	3.9	4.3

The results with rubber are accordingly similar to those with balata. The upper limit of the active radiations was here too about 400μ .

7. *Balata Irradiated through Screens to Determine the Active Wave Length in the Ultra-Violet.*—In the following experiments, the activity of certain radiations of the mercury vapor lamp were studied.

Table X shows that active radiations are distributed almost uniformly throughout the range of the ultra-violet. It is known that sunlight also contains ultra-violet radiations up to 300μ . It may be said, therefore, that active radiations of sunlight which cause the autooxidation of balata and of rubber lie between 300 and 480μ .

TABLE X
RELATIVE VISCOSITIES OF 0.2 MOLECULAR SOLUTIONS IN TETRALIN

	Balata Behind a Screen		Balata Behind a Screen		Balata Behind a Screen		Balata Behind a Screen		Balata Behind a Screen		Balata Behind a Screen		Balata Behind a Screen		Balata Behind a Screen	
	Quartz		Quartz		Quartz		Quartz		Quartz		Quartz		Quartz		Quartz	
	$\lambda >$		$\lambda =$		$\lambda =$		$\lambda =$		$\lambda =$		$\lambda = 313$		$\lambda >$		$\lambda >$	
	200 μ		436 μ		405 μ		366 μ		and 302 μ		400 μ		320 μ			
	70	20	70	20	70	20	70	20	70	20	70	20	70	20	70	20
	Cm.	Cm.	Cm.	Cm.	Cm.	Cm.	Cm.	Cm.	Cm.	Cm.	Cm.	Cm.	Cm.	Cm.	Cm.	Cm.
Not irradiated	7.1	7.4	7.1	7.4	7.1	7.4	7.1	7.4	7.1	7.4	7.1	7.4	7.1	7.4	7.1	7.4
8 hours ultra-violet	2.6	2.6	2.9	2.9	5.0	5.1	4.5	4.6	3.9	3.9	4.3	4.4	4.3	4.4	4.0	4.1

There is no avoiding the conclusion that if a colored substance is to exercise an inhibitory action on the autooxidation of rubber and of balata, it must not only be easily soluble in rubber and in balata, but must also absorb all radiations lying between 300 and 480μ .

Experimental Part

1. *Solvents.*—Since pure balata and rubber extracted with acetone are very sensitive to oxygen, all the solvents had to be carefully purified and freed of all traces of dissolved oxygen by distillation in an atmosphere of nitrogen.

For the viscosity measurements, tetralin was used. To purify the tetralin, it was treated with sulfuric acid and soda and was then preserved over sodium so as to avoid the formation of its peroxide.¹² Before it was used, it was distilled once more in an atmosphere of nitrogen, and was then passed by means of nitrogen under pressure into a burette from the flask where it had been collected. The quantity required in the preparation of the solutions was measured by the burette without letting the liquid come in contact with air.

2. *Preparation of Pure Balata, of Rubber Extracted with Acetone, and of the Acetone Extract of Rubber.*—The purified balata was prepared according to directions given in a preceding work,¹³ starting from balata latex. It was obtained by coagulation with alcohol or acetone. The coagulated product was dissolved in carbon tetrachloride, and the impurities were separated out by filtration. The balata was reprecipitated from these solutions by alcohol. By repeating this operation three times, and avoiding access of air to the greatest possible extent, pure balata was obtained in the form of a white fibrous product which was dried *in vacuo* to a constant weight.

As for the rubber, it was first precipitated from its latex by alcohol. The coagulated portion was then extracted with acetone for a week, the work being carried out in darkness with exclusion of air. The solvent was removed from the dissolved portion by evaporation. The residue was composed of a brown oily sub-

stance. It was this product which constituted "the acetone extract of rubber" used in the experiments. The rubber extracted with acetone was then extracted with ether. By precipitation of the ether solution with alcohol, there was obtained a rubber which was extremely sensitive to oxygen and which was used in our experiments. Ether extraction was necessary because not all of the rubber was entirely soluble in tetralin,¹⁴ although this liquid was required for the viscosity measurements. The rubber thus obtained was dried *in vacuo* to a constant weight.

3. *The Preparation of a Solid Mixture of Balata and of the Substances to Be Studied.*—The purified balata and other substance, the antioxygenic effect of which was to be studied were weighed in a test tube. The tube was then evacuated and refilled with nitrogen. With the aid of the burette mentioned earlier, benzene, freshly distilled in an atmosphere of nitrogen, was allowed to flow into the tube. The tube was then evacuated several times more, filling it each time with nitrogen, and finally it was sealed in an atmosphere of nitrogen. It was then agitated until solution was complete. The benzene was then removed *in vacuo*, and the solid residue was dried to a constant weight.

4. *Filtration of the Light.*—In order to filter sunlight, two tubes were placed one inside the other. The purified balata or rubber was placed in the inner tube and the solution of the substance acting as a filter was placed in the outer tube. The diameter of the outer tube was 12 millimeters and that of the inner tube was 8 millimeters, so that the thickness of the filtering solution through which the light had to pass before it reached the balata or the rubber was 2 millimeters.

For the experiments with ultra-violet light two quartz test tubes were used, fitting one inside the other. The diameter of the outside tube was 19 millimeters, that of the inside tube was 13 millimeters. The thickness of the filtering layer was 3 millimeters in this case.

5. *Preparation of Solutions for the Viscosity Measurements.*—The viscosities were measured before and after irradiation. To this end, the substance was weighed in the test tube, which had been evacuated several times, and the tube filled with nitrogen each time. The calculated quantity of tetralin (freshly distilled in an atmosphere of nitrogen) was then run into the tube from the burette. The liquid was solidified with the aid of a refrigerant, and the tube was evacuated several times, filling it each time with nitrogen and finally sealing it in an atmosphere of nitrogen. When completely dissolved, the solution was ready to be measured.

6. *Preparation of Solutions for Filtering Ultra-Violet Light.*¹⁵—A solution of 100 cc. of water, 0.0075 gram of rhodamine, 2 grams of quinine sulfate, 6 cc. of normal solution of sulfuric acid, allows 38 per cent of the radiation 436μ to pass through.

A solution of 100 cc. of alcohol, 0.03 gram of fuchsin and 4 grams of quinine chlorohydrate allows 34 per cent of the radiation of 405μ to pass through.

A solution of 100 cc. of water and 0.03 gram of fuchsin allows 31 per cent of the radiation 366μ to pass through.

A solution of 100 cc. of water, 0.0024 gram of potassium chromate and 0.0019 gram of nitrosodimethylaniline allows 30 per cent of the radiation of 313μ and 19 per cent of the radiation of 302μ to pass through.

Résumé

1. The problem involved in the present work was to learn whether, in addition to the known antioxygens which act chemically, there may not be colored substances capable of exercising an inhibitory action on the autooxidation of balata and of rubber by absorbing the active radiations which promote this autooxidation.

2. The substances to be studied were irradiated in the solid state and in the presence of air, either with sunlight or with ultra-violet light. Before and after irradiation, the degree of autooxidation was determined by measurements of the viscosity.

3. By mixing a few hydrocarbons and a few quinones with the balata, it was proved that bidiphenyleneethylene and β -naphthoquinone, which are highly colored, exert a highly antioxygenic action.

Others, like α -naphthoquinone, exert a highly polymerizing influence in addition to their catalytic action. This polymerization is still greater in the absence of air.

4. To eliminate all chemical influence, some experiments were carried out in which the light was passed through solutions of colored substances before reaching the balata or the rubber. In this way it was proved that all substances which show antioxygenic properties when mixed with balata retain this same property when they act as light filters. To this category of substances also belongs the acetone extract of rubber. The results are the same for balata as for rubber. Accordingly the question asked at the beginning must be answered in the affirmative.

5. In order to determine the length of the active radiation, the irradiation of balata was made through filtering solutions having a known range of absorption. In this way it was proved that the length of active radiations of sunlight lay between 300 and 480 μ . In the ultra-violet light region, the activity was distributed quite uniformly. It may be said, therefore, that a colored substance can greatly inhibit the autooxidation of rubber and of balata if it absorbs light between 300 and 480 μ and if it is easily soluble in rubber or in balata.

Acknowledgment

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The Effect of Surface-Active Substances and Electrolytes upon the Crystallization of Sulfur from Rubber Solutions

B. Dogadkin and J. Margolina

INSTITUTE OF THE RUBBER INDUSTRY, MOSCOW, U. S. S. R.

1. Theoretical Considerations

As technical practice has shown, the presence of large aggregates of sulfur in raw rubber mixtures can make vulcanized rubber goods not only defective but unusable. Although during vulcanization, solution of the sulfur in the rubber and a certain equalization of its concentration through diffusion take place, the large inclusions of sulfur are manifest, as has been shown by Graffe,¹ as centers of local overvulcanization which also lead to blooming of the sulfur and other defects in the products. This phenomenon is to be seen especially in the manufacture of thin-walled articles and fabrics, since the time required for vulcanization is in no way sufficient for the concentration of sulfur to become equalized throughout the volume where diffusion takes place.

In view of this latter fact, it is of particular interest to find a sure way of obtaining a uniform and low concentration of sulfur upon drying a rubber cement containing sulfur. Among other things, the mechanical process of mixing the rubber determines the character of the distribution, a problem which has been discussed by Graffe,² Burowaja,³ and others. Our investigation takes up the problem from another point of view, that is, the possibility of modifying the crystallization process of sulfur in cements by the introduction of substances with special chemical properties.

In the selection of these substances, it was first of all necessary to consider in a general way the phenomenon of condensation during the formation of a new phase. The process of crystallization from solutions has been described in works by Mark,⁴ von Weimarn,⁵ and others. According to these investigators, the crystallization process falls into two stages. During the first stage there are formed in the solution centers of crystallization or "nuclei" of ultramicroscopic size. During the second stage of the actual crystallization process, the nuclei grow as a result of diffusion of the molecules (or ions) of the solute from the solvent to the surface of the nuclei. According to von Weimarn the rate of the formation of the nuclei is defined by the equation:

$$W = K \frac{Q - L}{L}$$

where Q is the total quantity of dissolved substance and L its solubility during crystallization. The constant K depends upon a series of conditions, particularly upon the over-all dimensions of the molecules of the substance which is being condensed, and upon the viscosity of the solvent. The rate of growth of the nuclei is expressed by the well-known equation of Noyes-Nernst:

$$V = \frac{D}{\delta} O(C - l)$$

where D is the coefficient of diffusion, δ the distance of diffusion, O the surface of the nuclear crystal, C the concentration, and l the solubility of the crystal at the particular degree of dispersion.

It is evident that the greater the rate of growth of the nucleus W (based on the number of nuclei which are formed in a given time), the finer and more uniform will be the precipitate under otherwise equal conditions. On the other hand, the increase in the rate of growth V of the individual crystals leads to the formation of a coarse crystalline precipitate. In this way it is theoretically possible to control the crystallization process and to obtain crystals of any desired size.

However, in practice such a control of simultaneous and interdependent processes is very difficult; for a comparison of the two equations shows that an increase in the degree of saturation of the system accelerates both processes. As the results of numerous experiments by von Weimarn have shown, the first process predominates over the second only for high states of saturation ($Q - L$), and also for low values of the solubility L , whereby a finely crystallized precipitate is obtained, *e. g.*, the formation of gels of calcium phosphate which are obtained by mutual decomposition of concentrated solutions of calcium chloride and sodium phosphate. If, however, the saturation value ($Q - L$) and ($C - l$) is low and granted that there are no significant changes in one direction or the other, there are very narrow limits to the influence of the crystallization process upon a change in the saturation of the system.

This was confirmed by our experiments. We investigated the crystallization of sulfur in rubber solutions with various solvents, including benzine, benzene, toluene, xylene, and carbon disulfide. It might be expected that with a change in the solubility L , the saturation value ($Q - L$) would also change upon evaporation of rubber-sulfur solutions of concentration C . However the differing solubility of the sulfur in the liquids mentioned was only to a slight degree evident in the size of its rhombic crystals. The influence of the solvent was most evident in the crystallographic character of the precipitate.

Further light was thrown on the problem by experiments which were directed toward establishing the influence of certain substances on crystallization. As has already been mentioned, the constant K in the equation of von Weimarn depends upon the molecular size of the substance to be crystallized. In general, nuclei formation in solutions of low molecular weight is difficult. Particularly favorable conditions are required for temporary molecular aggregates to form at definite spatial points, whose combination might lead to nuclei of ultra-microscopic dimensions. Therefore crystallization of such a substance takes place first in the vicinity of stray foreign inclusions, which act as centers of crystallization. Molecules of substances with high molecular weight may act as such nuclei. The more they are in a position to form "colonies" and other molecular groups, the greater is their condensing action. Polar molecules in particular have the capacity to form "colonies." It is known that molecules of all surface-active substances belong to this class of molecules.

Although the action of surface-active substances is to promote nuclei formation and to accelerate the first stage in the formation of the precipitate, these substances retard the progress of the second stage, that is, the growth of crystals. They are absorbed on the surface of the nucleus as well as on the surface of the small crystals, they saturate the forces of the crystalline lattice and in this way disturb the normal deposition of the substance on the crystals by means of diffusion. At the same

time the presence of the adsorption film prevents nuclear aggregation as well as any possible diminution in the number of nuclei.

This effect of an organic substance on the process of crystallization was studied by Mark and Wenk.⁷ They showed that the crystallization of potassium sulfate in the presence of quinoline yellow is retarded or wholly prevented. In the first case the potassium sulfate crystals are visibly colored with the adsorption layer of pigment. The adsorptive character of the effect of quinoline yellow is also confirmed by the way in which the rate of crystallization is related to the concentration of color in the solvent. This relation is expressed by the equation

$$g = \log \frac{V_0}{V} = KC^{1/n}$$

where V_0 is the rate of crystallization (not in the presence of a pigment) and V the velocity at concentration C .

Based on these considerations, therefore, the desired influence of surface-active substances soluble in benzene on the phenomenon of sulfur crystallization is to be expected. In their presence, the precipitate of sulfur must consist of a large number (corresponding to the largest number of centers of crystallization which appear in the first stage) of uniformly dispersed small crystals (corresponding to the low velocity of the second stage). The experiments carried out in the present work confirm this assumption.

2. Experimental Part. The Effect of Surface-Active Substances

The experiments were carried out in the way described below. Following the usual methods, a mixture of 100 grams of rubber and 8 grams of sulfur was worked on the mill at 60–70° C. The mixture was then dissolved in benzene at room temperature in the proportion of 1:6. The rubber solutions thus obtained were placed in the form of thin films on a microscopic slide; the benzene was evaporated and the process of crystallization of the sulfur was observed under the microscope. The best preparations were photographed in a Zeiss-apparatus with transmitted light, with a magnification of 90-fold. The reproductions show the microphotographs magnified only 45 times. The photographs give clear pictures of the precipitates, as well as the character of the crystals and their size. All the experiments were carried out with two kinds of sulfur, *viz.*, flowers of sulfur and ground sulfur. There was no difference in the behavior of the two kinds of sulfur.

The surface-active substances to be studied were added either to the benzene or to the rubber, during the preparation of the mixtures. The manner of introduction was without any apparent effect on the character of the action of these substances. The substances which were studied included technical fish oil, rosin, stearic acid, oleic acid, zinc oleate, calcium oleate, thionaphthenic acid, and alkali sulfate. They were used in proportions from 0.5 to 5 per cent, based on the rubber.

As the accompanying photographs show, all these substances decreased the size of the sulfur crystals which were precipitated during the drying of the cement films. This is particularly clear by a comparison of Figs. 1 and 3. In Fig. 1 the sulfur is precipitated out of a rubber solution containing only sulfur and rubber; the precipitate shown in Fig. 3 is from a rubber solution containing 1 per cent of fish oil, based on the rubber. In the first case the maximum dimensions of the average crystals was roughly 44.4 μ , and in the second case at 5.0 μ . Simultaneously with the change in the size of the crystals, their shape changed and they became rounded. This shows beyond doubt the formation of adsorption layers of surface-active

substances on the edges of the growing crystals. The adsorption is most pronounced at the edges with the greatest strain of the lattice forces, where the growth is chiefly retarded. As a consequence, new slowly enlarging edges are formed on the crystals, causing the crystals to become round.

The action of the various surface-active substances is seen clearly in the following table. The size of the crystals is expressed as the reciprocal ($1/n$) of the number (n) of crystals in 1 square centimeter of the visible field at a magnification of 90-fold. Naturally this value should be used only for qualitative comparisons. The dispersion of the substance corresponds to the extent of its effect upon the crystallization of sulfur, *i. e.*, its diminution of the size of the crystals. It should be added, however, that the differences in the effect of surface-active substances were very small.

TABLE I

Substance	Method of Introduction	Quantity (Based on the Rubber) in Per Cent	Number of Crystals in 1 Sq. Cm. of the Field of Vision $\times 90$	$\frac{1}{n}$	Maximum Size of Average Crystals in μ	Number of the Photographs
1. Technical fish oil	As a paste with sulfur	1.0	17	0.06	5.0	3
2. Thionaphthenic acid	By calendering into the rubber	1.5	12.8	0.08	6.0	12
3. Naphthenic acid	By calendering into the rubber	1.5	11.0	0.09	6.2	13
4. Calcium oleate	By calendering into the rubber	1.5	7.8	0.12	7.1	14
5. Rosin	As a paste with sulfur	5.0	7.27	0.13	...	15
6. Vaseline oil	By calendering into the rubber	2.0	2.1	0.5	...	9
7. Machine oil	By calendering into the rubber	2.0	2.3	0.44
8. Sodium chloride	In benzine	Traces	8.2	0.18	8.2	10
9. Sodium bicarbonate	In benzine	Traces	8.8	0.11

According to the results of the analytical laboratory of the Research Institute of the Rubber Industry the fish oil had the following properties: saponification no. 200, acid content 13, iodine number 94, nitrogen-containing substances (calculated as protein) 2.18%, ash 1.67%.

As was to be expected, the effect of surface-active substances depends upon their concentration. In the experiments with fish oil, the smallest crystals were observed in the case of a rubber solution containing 1 per cent of fish oil (based on the rubber). An increase in concentration led to an increase in the size of the sulfur crystals, so that at 3 per cent concentration the precipitate consisted of crystals which were larger than in the original rubber solution containing no surface-active substance. This is confirmed by Table II and Figs. 2 to 5.

TABLE II

Content of Fish Oil in the Rubber Solution in Per Cent (Based on the Rubber)	Number of Crystals in 1 Sq. Cm. of the Field of Vision $\times 90$	$\frac{1}{n}$	Maximum Size of Average Crystals in μ	Number of the Photographs
0	1.58	0.63	44.4	1
0.5	3.56	0.28	..	2
1.0	17.0	0.06	5.0	3
2.0	10.8	0.09	..	4
3.0	0.70	1.43	55.5	5

One may therefore speak of an optimum concentration of the dispersing effect of surface-active substances. We are not in a position to give a rational explanation of these facts, which are so important from a technical point of view. One can only refer to the analogous action of capillary-active substances in the case of the stabilization of aero sols of ammonium chloride.⁸

The following observation appears to be of no less importance from a technical point of view. It was observed that the dispersing action of surface-active substances diminished upon storage of rubber solutions. Figures 3, 6, and 7 show deposits of sulfur which were formed under the same conditions from the same rubber solution (containing 1 per cent of fish oil), but after various lengths of time following the preparation of the rubber solutions. The size of the sulfur crystals increased in proportion to the aging of the rubber solutions. Upon storage of the rubber solutions for 144 hours in sealed white glass vessels an uneven deposit was formed, the individual crystals of which were larger than the crystals of the original rubber solutions containing no surface-active substances (Fig. 7). If the dispersing action of surface-active substances is to be utilized in technological practice, either freshly prepared rubber solutions (which have not stood longer than 72 hours) must be used, or these substances must be introduced in solution into the finished cements directly before use.

The change in the influence of surface-active substances which takes place in the course of time is common to all the substances studied by us. A few of them, *e. g.*, oleic acid and stearic acid, are more stable than the others in this respect. At a concentration of 1 to 2 per cent, the dispersing action showed a marked diminution only after 7 days. Other substances required other times, according to the concentration. Nevertheless the general character of this phenomenon proves that the diminution in the action with time is connected not only with changes in the surface-active substances themselves, but with a change in the system as a whole. Obviously the aging of rubber itself plays a not unimportant role. It is also probable that in the course of time an important part of the surface-active substances is directly bound to the rubber (adsorption), and in this way enters into the reciprocal action with sulfur. This opinion is substantiated by the following experiment. If a fresh quantity of surface-active substance is added to an old rubber solution in which the dispersing effect of the surface-active substance is no longer manifest, the precipitated layer again acquires a fine crystalline structure.

It is worthy of note that, upon storage of rubber mixtures, a diminution in the action of surface-active substances was not observed. Figure 8 shows the precipitate obtained from a mixture containing 1 per cent of fish oil which was stored for 2 months under ordinary conditions. There was no noticeable crystallization of the precipitate in the films on the glass.

The specific action of surface-active substances is confirmed by experiments which show the phenomena of the crystallization of sulfur from a rubber solution containing machine and vaseline oils. Those rubber softeners which promote the dispersion of sulfur in rubber and contain no substances with polar groups in them, do not reduce the size of crystals of precipitated sulfur. Figure 9 shows the precipitate of sulfur for a 2 per cent content of one of these substances. The crystals of the precipitate are distinctly larger than the crystals obtained from cements of the original mixtures.

3. The Action of Electrolytes

It is well known that some electrolytes in non-associated liquids (benzine, benzene, etc.) tend to form colloid solutions. Even a low concentration of these

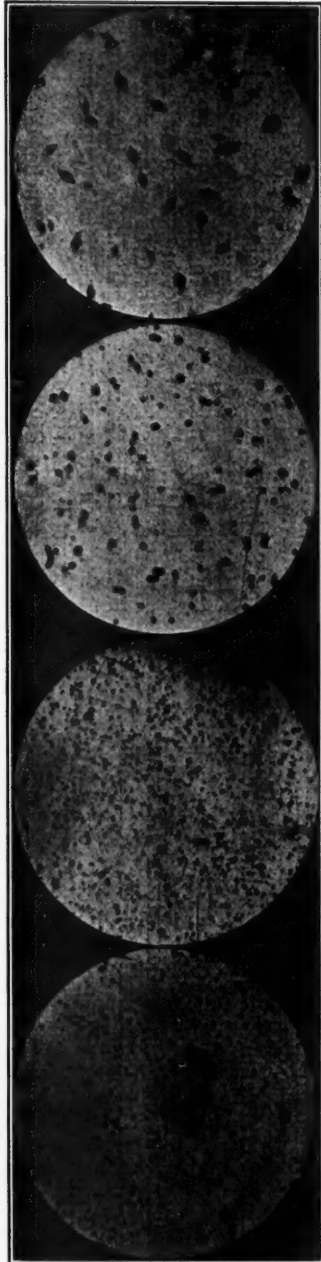


Figure 1
Rubber + sulfur in benzene
X 90

Figure 2
Rubber + sulfur + 0.5% fish oil
in benzene. X 90

Figure 3
Rubber + sulfur + 1% fish oil
(The solution was preserved 24
hours.) X 90

Figure 4
Rubber + sulfur + 2% fish oil
in benzene. X 90

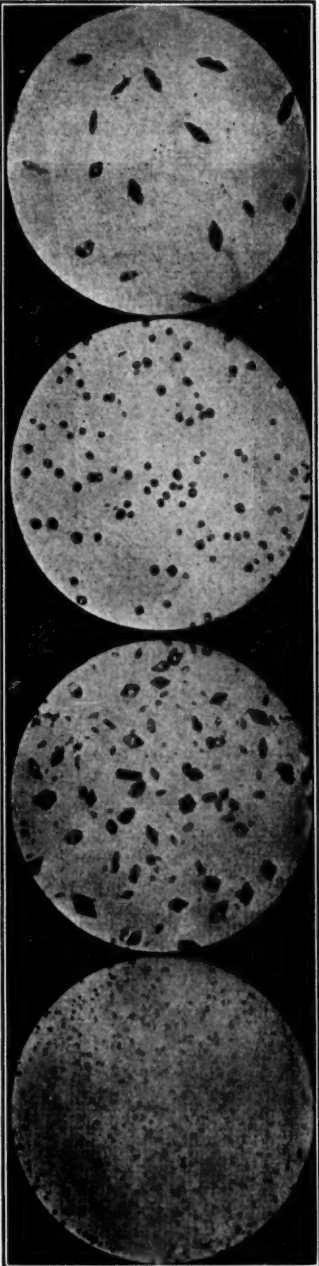
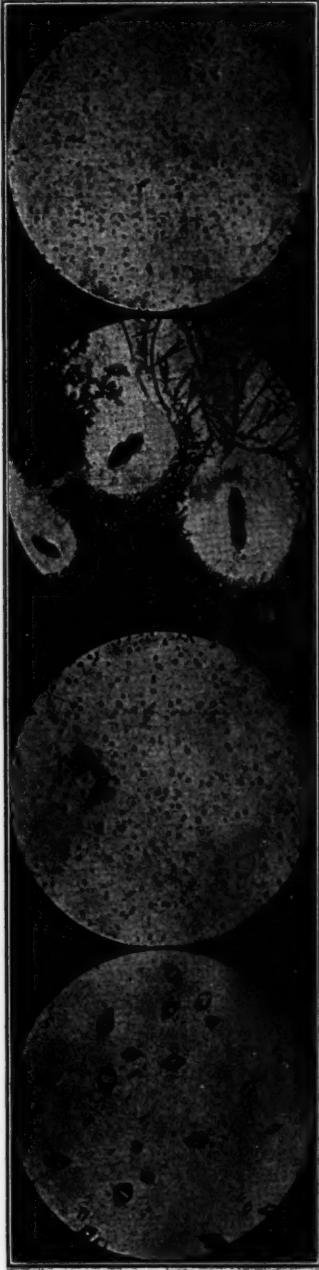


Figure 5
Rubber + sulfur + 3% fish oil
in benzene. X 90

Figure 6
Rubber + sulfur + 1% fish oil
in benzene (The solution was
preserved 96 hours.) X 90

Figure 7
Rubber + sulfur + 1% fish oil
in benzene (The solution was
preserved 144 hours.) X 90

Figure 8
Rubber + sulfur + 1% fish oil
in benzene. (After 60 days.) X
90

**Figure 9**

Rubber + sulfur + 2% vaseline
oil in benzene. $\times 90$

Figure 10

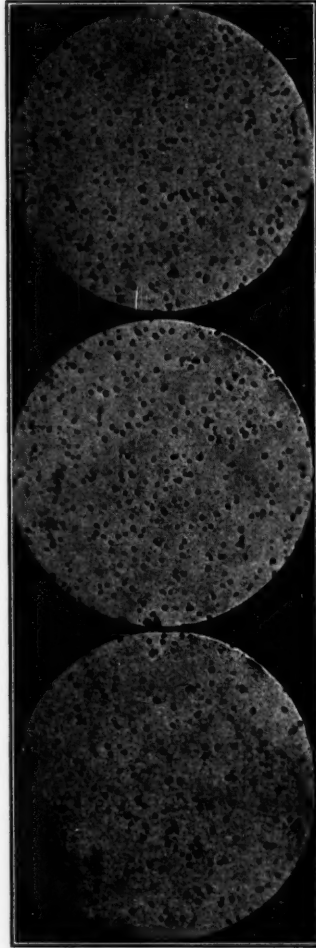
Rubber + sulfur + trace of NaCl
in benzene. $\times 90$

Figure 11

Rubber + sulfur + 1% fish oil
in benzene. (The microscope slide
warmed to 70° C.)

Figure 12

Rubber + sulfur + 1.5% thio-
naphthenic acid in benzene. $\times 90$

**Figure 13**

Rubber + sulfur + 1.5% naph-
thenic acid in benzene. $\times 90$

Figure 14

Rubber + sulfur + 1% calcium
oleate in benzene. $\times 90$

Figure 15

Rubber + sulfur + 5% rosin in
benzene. $\times 90$

electrolytes leads to the formation of aggregates, the size of which lies within the range of 1 to 100 μ . It is our opinion that these aggregates may act as numerous centers of crystallization for sulfur, similar to the phenomena in the experiments by Zsigmondy,⁹ where the sub-microscopic gold particles formed in the reduction by means of phosphorus serve as centers of crystallization for silver and other metals.¹⁰ We carried out experiments on the crystallization of sulfur with rubber solutions consisting of the base mixture of rubber and sulfur described above, using as solvent benzine saturated with the following electrolytes: calcium chloride, sodium chloride, potassium bromide, lithium chloride, sodium bicarbonate, and lead acetate. In all instances the crystals of the precipitate were considerably smaller than the crystals from mixtures with no electrolyte (see Table I and Fig. 10). Sodium chloride had the greatest effect, sodium bicarbonate and calcium chloride the least. The precipitate of sulfur obtained in the presence of sodium chloride resembled in outward appearance the precipitate of sulfur from a rubber solution containing fish oil, obtained under similar conditions.

4. The Effect of the Temperature

A change in temperature influences the rate of condensation in both stages. Depending upon the sign of the heat effect of crystallization, an increase in temperature can either accelerate or retard the second stage, that is, the process of growth in the crystals. As far as the first stage, the formation of the nuclei, is concerned, there is from all appearances a certain critical value of the osmotic pressure P_k , at which the process of nuclei formation commences. The value P_k is a function of the temperature, and can be expressed by an equation similar to the equation for the condensation upon hard surfaces from the gaseous phase:

$$P_k = D e^{\frac{-U_s}{RT}}$$

where D is a constant and U_s is the heat of the solvent.

Based on this equation for the crystallization of sulfur, it might be expected that an increase in the temperature of evaporation of the benzine solvent would lead to an increase in the size of the crystals (a decrease in the number of centers of crystallization). As a matter of fact, it was proved that the dispersing action of surface-active substances takes place if the microscopic slide is heated to 70° C. before the rubber solution or the film is placed on the glass. Under these conditions the progress of crystallization undergoes a sudden change. Rubber solutions, both when they contain the substances mentioned above and when they do not, give films in which the sulfur crystallizes in the form of monoclinic and rhombic dendrites, with large crystals in the rhombic system (Fig. 11). An increase in content of capillary-active substances up to about 5 per cent does not change the course of this crystallization.

If, therefore, it is desired to utilize surface-active substances in order to diminish the size of sulfur crystals, careful attention must be paid to temperature conditions. There is no doubt that the effect of the temperature on the course of crystallization varies according to the composition of the surface on which the rubber solution is placed.¹¹

5. Experiments with Technical Mixtures

In order to confirm the behavior of the substances already mentioned in technical mixtures, experiments were made with one of the mixtures used at the rubber works in Moscow for rubberizing cloth. The mixture and the rubber solution were prepared under conditions which reproduced the factory conditions as far

as possible. The results of these experiments strengthen the assumption that the use in technical mixtures under definite temperature conditions of the substances mentioned can be of considerable value, since in this way the formation of large sulfur crystals in cements and spreading mixtures can be prevented.

6. Conclusions

1. If surface-active substances are added directly to rubber or to the solvent *e. g.*, fatty acids and their salts, naphthenic acids, thionaphthenic acids, etc., there is after evaporation of the solvent a marked reduction in the size of the sulfur crystals which are formed in the rubber films.

2. The size of the sulfur crystals depends upon the concentration of the surface-active substances in the rubber solution. The precipitate with the greatest degree of dispersion is obtained at a definite optimum degree of concentration, *e. g.*, one per cent of calcium oleate and fish oil, based on the rubber. A higher concentration of surface-active substances leads to an increase in the size of the sulfur crystals.

3. The dispersing action of capillary-active substances decreases with the age of rubber solutions, but this was not observed after storage of the mixtures and films themselves.

4. Rubber softeners in the molecules of which there are no polar groups (*e. g.*, vaseline oil) show no dispersing action.

5. Some electrolytes, added to the rubber solution, likewise promote the dispersion of sulfur in the form of small crystals.

6. The dispersing action of surface-active substances and electrolytes disappears with an increase in the temperature at which the film is formed (up to 70° C.). The sulfur is precipitated in the form of monoclinic dendrites and rhombic crystals.

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Viscometric Studies of Rubber Solutions

Markus Reiner

JERUSALEM

A former communication¹ reported viscometric observations on rubber-toluene solutions in different capillary and rotation viscometers. The consistency curve of solutions from 0.08 to 1.77 per cent concentration starts at the origin as a straight line, inclined at a definite angle until it reaches a certain point *a* (see Fig. 1). From there it becomes convex toward the stress axis. This convex part extends to an inflection point *b* where the curve becomes concave up to a point *c*, where it again becomes a straight line which by extrapolation passes through the origin. The solutions therefore behave as Newtonian liquids between points *o* and *a*, and *c* and ∞ . Between point *a* and *c* they are non-Newtonian liquids.

It was furthermore shown that the "relative" consistency curve, *i. e.*, a curve in which the shearing stress is reduced or the rate of shear increased in proportion to the viscosity of the solvent, is independent of the temperature at which the viscosity measurement is made. From this latter property the conclusion was drawn that the phenomenon of non-Newtonian behavior is a purely mechanical one. It cannot be due, as has been suggested by Staudinger,² to a competition between orientation due to laminar flow and rotational diffusion due to Brownian movement because the magnitude of the latter depends on the temperature.

The independence of the temperature also rules out the assumption of an adsorption layer of variable thickness proposed by others, because the thickness of such an adsorption layer can hardly be independent of the temperature. It was accordingly concluded that the non-Newtonian behavior must be due to the rubber particles in solution being "gel fragments" or secondary particles "permeated in gel-like fashion with the liquid medium," as suggested by Kraemer and Williamson.³ This model explains the existence of point *a*. It is defined by the strength of the bond between the primary particles or structural elements. Until the stresses produced in the secondary particles by the flow-deformation reach this breaking strength, the solution must naturally behave as a Newtonian liquid. When the shear is increased beyond this point, the secondary particles are broken up to form primary particles, releasing at the same time liquid medium. This increases the fluidity of the solution and causes the curve to become convex. The fragments formed through the process just described reaggregate when coming in contact in the course of flow, and a dynamic equilibrium may establish itself between the disaggregation and reaggregation.

According to the bond which operates between the primary particles, the secondary particles can be either macromolecules, micelles, ordered or unordered groups. The first three types however have the property in common that the fragments will not reunite at every chance encounter, but only when they meet in certain orientations to each other. As a result, a time-lag should be observed if a closed consistency curve were described, *i. e.*, the consistency curve should show a hysteresis loop. This was not found to be the case by our observations. Regardless of whether the rate of shear was being increased or decreased, the observational points fall upon a single smooth curve. This excludes the possibility of ordered aggregates, and therefore leaves only the possibility of unordered aggregates of primary

particles, held together by cohesive forces, the primary particles themselves being either macromolecules, micelles, or ordered groups. These preliminary conclusions drawn from the observations were purely qualitative. In the present paper we will treat some of our experimental data quantitatively.

The quantitative relation which is most commonly looked for in viscometric observations with solutions of different concentrations is one between viscosity and concentration. When, however, a non-Newtonian liquid flows through a tube (or any other viscometer), there prevails in each telescopic layer a different rate of shear and therefore a different viscosity. It is therefore generally impossible to speak of the viscosity of the liquid at a certain efflux, corresponding to a certain point on the consistency curve. While rubber-toluene solutions are generally non-Newtonian liquids, it was found that there exist two regions in which the solutions behave as Newtonian liquids. In these regions definite constant viscosities therefore exist, which we may denote by η_0 and η_∞ .

The viscosity, η_0 , at rest and up to the point *a* may be called the "zero viscosity." The relative zero-viscosities of different solutions were determined from our observa-

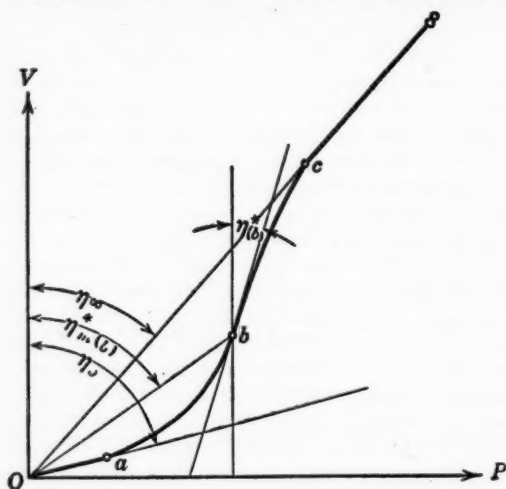


Figure 1—General Shape of the Consistency Curve

tions, and are shown in Table I. Table I also shows the "specific" viscosity, which is defined by

$$\text{specific } \eta = \text{relative } \eta - 1 \quad (1)$$

TABLE I
RELATIVE AND SPECIFIC ZERO-VISCOSITIES AND FLUIDITIES

Concentration	No. of Solution							
	11	19	7	6	4	3	2.1	2
$10^3 c_v$	1.71	1.48	0.98	0.97	0.23	0.17	0.11	0.08
rel η_0	185	108	36.2	27.3	2.55	2.15	1.76	1.60
rel η_∞	.00541	.00943	.0276	.0366	.3922	.4651	.5681	.625
spec η_0	184	107	35.2	26.3	1.55	1.15	0.76	0.60
a_0	10800	7240	3600	2700	670	680	690	750

and *a*, the specific viscosity per unit of concentration, i. e.,

$$a = \text{specific } \eta / c_v \quad (2)$$

where c_v is the volume-concentration of the solution.

In Fig. 2 $\text{rel } \eta_0$ and a_0 have been plotted as functions of c_v . As can be seen from this figure, $\text{rel } \eta_0$ is linear and a_0 constant up to $c_v = 0.3$ per cent, corresponding to a value of $\text{spec } \eta_0 = 2$. This is remarkably high, as it is usually assumed that with solutions of high molecular substances the simple linear relationship had its limit with $\text{spec } \eta_0 = 0.3$.⁴ The constant value of a_0 is 700. This can be interpreted as follows: (a) For very dilute suspensions of spherical particles Einstein derived the formula:

$$\text{specific } \eta = 2.5C_v \quad (3)$$

where C_v is the concentration of the suspended particles. If the suspended particles are solvated, *i. e.*, if they immobilize part of the dispersion-medium, we have

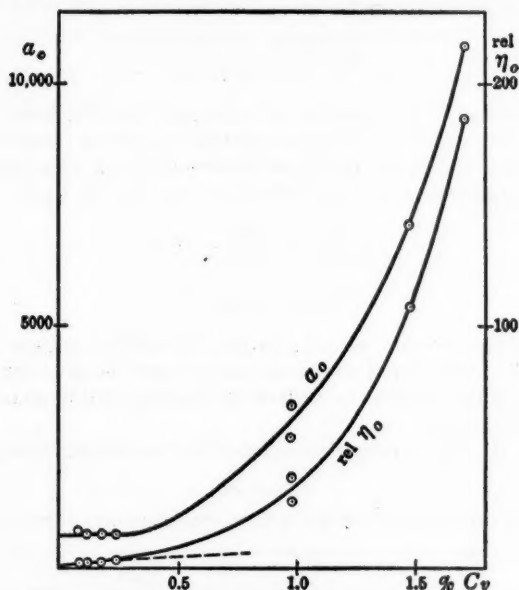


Figure 2—Relative Zero Viscosities for Different Concentrations

$$C_v = bc_v \quad (4)$$

where $b > 1$. b has been called the specific hydrodynamic volume of the material.

Introducing the value for C_v from (4) into (3) we get

$$\text{specific } \eta = 2.5bc_v \quad (5)$$

and by considering (2)

$$a = 2.5b \quad \text{or} \quad b = a/2.5 \quad (6)$$

In our case we would have

$$b_0 = 700/2.5 = 280 \quad (7)$$

i. e., if the dispersed solvated rubber particles were of a spherical shape, the volume of the immobilized liquid would be 279 times the volume of the dispersed rubber and the particle concentration of our solutions, 2, 2.1, 3, and 4 would be 22, 31, 48, and 65 per cent, respectively. This however, is not possible. Einstein's equation is

valid for very dilute solutions only, and it is well known that the viscosity increases linearly with concentration at small concentrations only. As has been said before, the increase of viscosity is linear and quite small up to $c_v = 0.30$ per cent.

If the real concentration corresponding to $c_v = 0.30$ per cent were $280 \times 0.3 = 84$ per cent, this would be out of question. The actual ratio of volume of immobilized liquid to volume of rubber must therefore be much smaller than 279. (b) Einstein's formula⁵ (3) can be generalized to

$$\text{specific } \eta = AC_v \quad (8)$$

for particles of general (non-spherical) shape, where A is a different constant for every different shape of the particle, being equal to 2.5 in the case of a sphere. Eischitz⁶ could show that under certain assumptions

$$A = \frac{1.15}{\pi} \cdot \frac{l}{d} \cdot \frac{1}{\ln l/d} \quad (9)$$

in the case of very long rotational ellipsoids of length l and thickness d .

If c_v were the true volume concentration of the dispersed phase, i. e., if the dispersed rubber was not solvated, and if we had reasons to assume that the particles are long rotational ellipsoids, we could calculate from Eq. (9) that

$$\frac{l}{d} \cdot \frac{1}{\ln l/d} = \frac{700\pi}{1.15} = 1910 \quad (10)$$

or

$$l/d = 20,000 \quad (11)$$

which means that the particles were of a length of 20,000 times their thickness. We know, however, that this cannot be the case, as the particles are solvated. We have therefore to picture the particles as solvated to less than 279 times and elongated to less than 20,000 diameters.

Table II shows possible combinations of solvation and elongation. Under C_v the

TABLE II
POSSIBLE COMBINATIONS OF SOLVATION AND ELONGATION FOR $a = 700$

l/d	280	100	10	1
C_v	84%	30%	3%	0.3%

particle concentration up to which the viscosity concentration relation is linear, is shown. Beyond this, we cannot at this stage draw any conclusions about the shape of the particle and the quantity of liquid imbibed.

This is how far the information provided by the first straight part of the consistency curve up to point a carries us. Next the establishment of a relation between the position of the point a and the concentration may be undertaken.

We said that the existence of a point a (Fig. 1) must be interpreted as indicating the starting of a mechanical disaggregation of the suspended rubber particles, through the breaking off of primary particles. This breaking off is caused by the stresses produced in the particle through the flow of the solvent when these stresses exceed the breaking strength β of the particles. We know from our data (see Fig. 3) the shearing stress (\bar{P}) and relative rate of shear (\bar{V}_{rel}) at which a is reached in the case of some of the solutions, and it should be possible to find a relation between these magnitudes and the breaking strength of the particle. Such a relation can be theoretically derived on the basis of Einstein's calculation of the viscosity of a solution. The result is as follows: Let \bar{V}_{rel} be the relative shearing velocity of laminar

flow, then a tensional stress, S_t , is developed in the particle, the magnitude of which is

$$S_t = n\bar{V}_{rel} \quad (12)$$

where n is a numerical factor, which in the case of spherical particles is equal to 5, and for "elongated" particles is greater than 5. The stress acts in a direction inclined under 45° against the direction of flow. It is independent of the concentration, the size of the particle and is the same in every point of the particle.

The particle begins to disaggregate as soon as S_t reaches the breaking strength β . Disaggregation will therefore start at the limiting relative shearing velocity

$$\bar{V}_{rel} = p/n \quad (13)$$

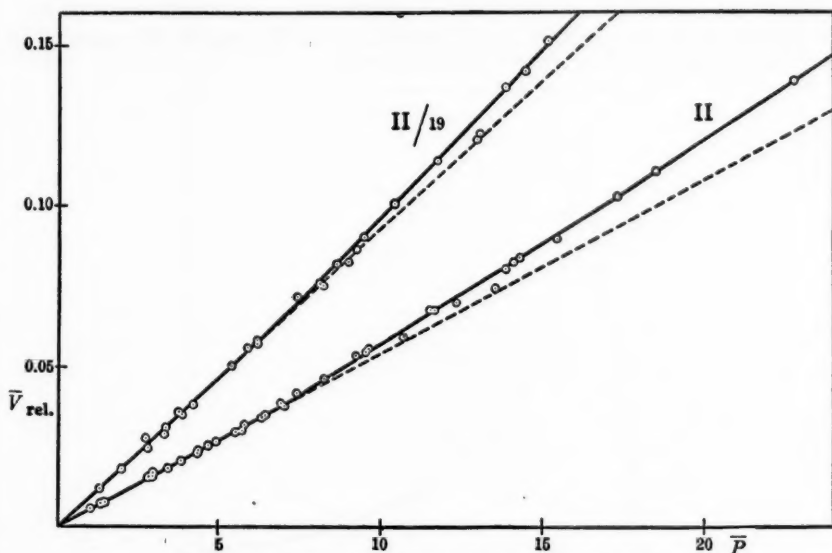


Figure 3—Consistency Curves at Low Rates of Shear

The limiting relative shearing velocity is therefore independent of the concentration.

On the other hand \bar{P} , the limiting shearing stress, is

$$\bar{P} = \eta_{rel} \bar{V}_{rel} = (p/n)\eta_{rel} \quad (14)$$

and as η_{rel} depends on c_v , \bar{P} depends in the same way on c_v . This seems not to be confirmed by Fig. 3. Here it looks as if on the contrary \bar{P} was independent of c_v and \bar{V}_{rel} was decreasing accordingly. It should, however, be borne in mind that the consistency curves (Fig. 3) refer to the solutions II and 19 with the high concentration of 1.71 and 1.48 per cent. For such concentrations our Equations (13) and (14) are not valid. Unfortunately, in the more dilute solutions the point a could not be reached at the maximum shear produced in the Couette apparatus.

Solutions II/2 and II/18, both with the same concentration of 0.08 per cent, were however, measured in the Couette and Bingham viscometer, and it was therefore thought possible to find \bar{P} and \bar{V}_{rel} by a graphical comparison of the measurements in both instruments. Such a graphical comparison is made difficult by the fact that

the shear produced in the capillary instrument is so much larger than the shear produced in the rotation instrument that a graph as usually plotted becomes unwieldy. This difficulty is partly overcome by plotting on a logarithmic scale. In the same way the measurements of solution III/14 and 13 and II/15 in the Bingham instrument were compared with the hypothetical between the measurements in a Couette instrument derived by interpolation between the measurements made with solutions II/17, II/6, II/4, and 3. The results are shown in Table III and in Fig. 4.

TABLE III^a

No. of Solution	II	19	14	13	15	18
$10^2 c_v$	1.71	1.48	0.39	0.38	0.21	0.08
\bar{V}_{rel}	0.034	0.058		2.55	7.79	7.35
\bar{P}	6.30	6.30		13.5	22.7	11.0

^a Because of the method used in the determination of \bar{V}_{rel} and \bar{P} , the values given for solutions 13, 14, 15, and 18 are very approximate.

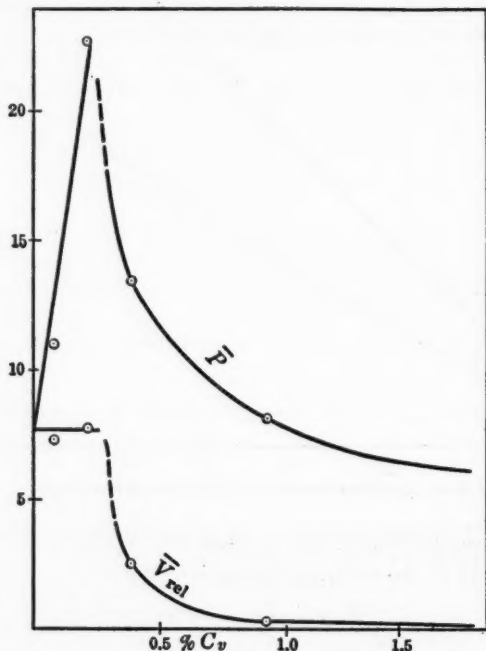


Figure 4—Limiting Rates of Shear and Shearing Stresses

Figure 4 confirms our Equations (13) and (14) for very dilute solutions. At concentrations over 0.25 per cent, however, both \bar{V}_{rel} and \bar{P} fall rapidly, the latter tending toward a constant. The concentration of 0.25 per cent is also approximately the concentration at which \bar{V}_{rel} ceases to increase linearly (see Fig. 2), i. e., this is the concentration at which the suspended particles influence one another in their hydrodynamic behavior. It may be expected that such an influence should bring with it a rapid decrease of \bar{V}_{rel} and \bar{P} .

The results of the preceding section confirm our interpretation of the point *a* of the consistency curve and therefore also of our model for the suspended particle and

the mechanism of the non-Newtonian behavior. For very dilute solutions \bar{V}_r tends to become constant with the value 7.70. According to Equation (13) we have

$$\beta = 7.70n \text{ dynes per sq. cm.}$$

We do however not know n , as we do not know the shape of the particle and are therefore not in a position to calculate β , the breaking strength of the suspended particles. This breaking strength is not identical with the cohesion of the rubber because in the solution the cohesion forces in the rubber are counteracted by the adhesion between rubber and solvent. Moreover the inclusion of the solvent reduces the massive section of the particle. It is not possible to calculate this reduction, as we do not know the volume of the solvent which is immobilized by the rubber particles. We can nevertheless say that the bond between the primary particles, as measured by β , is very small. If we take $n = 5$ we get $\beta = 38$ dynes per sq. cm., and this is about 10^{-7} the tensional strength of rubber. It can hardly be assumed that n should be so large as to make up this difference. We must there-

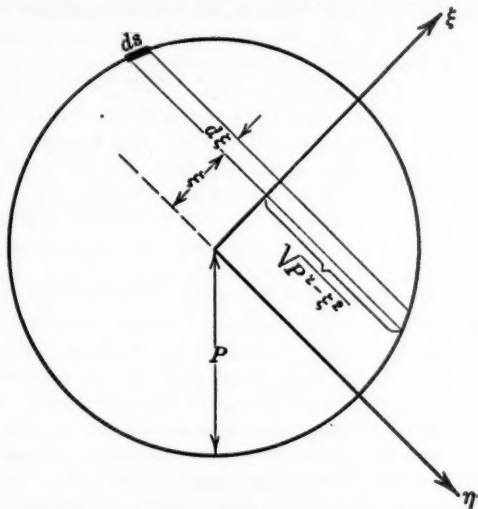


Figure 5—Stresses in a Spherical Particle

fore conclude that the forces which combine the primary particles to the secondary particles are very small.

The present quantitative analysis of the results of viscometric measurements with rubber-toluene solution has furnished new support for the model of solvated un-ordered aggregates, suggested for the suspended rubber particles. It was however not possible to calculate the amount of immobilized solvent, and therefore also not the size of the suspended particles. It is thought that this can only be accomplished by combining some other measurements with the viscometric measurements as, e. g., diffusion measurements.

I am glad to express my gratitude to E. C. Bingham for the interest taken in this research and to those benefactors who have made it possible.

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The Measurement of the Plasticity of Rubber

A Reply to Dillon and Johnston

J. Behre

In a recent contribution¹ Dillon and Johnston commence by criticizing my explanation of the dependence of the plasticity upon the pressure. They state that the shear dv/dx is dependent upon the shearing stress F and the slippage S , and that the pressure is not a criterion of the flow conditions of rubber. This is certainly true, and I have never maintained that the pressure is a criterion of the plasticity, but I certainly do use, as these authors also propose, the shear as a measure of the degree of plasticity, that is, the volume extruded in fifteen minutes. Naturally this depends upon the pressure or its component, the shearing stress. The only difference in the methods of measurement seems to me to lie in the magnitude of the shear and in the pressure applied. I do not believe that this leads to results which differ essentially, but differ only in their order of magnitude.

Furthermore, Dillon and Johnston believe that when I quoted my earlier publication² an error was made. This is not the case, for the graph in the work by Bachmann, Behre, and Blankenstein³ shows clearly the dependence of the work expended upon the degree of plasticity for both cold and hot mastication, and also shows that in order to reach a given plasticity, the amount of energy consumed during hot mastication is less than during cold mastication. The graph shows at the same time, however, that hot mastication makes rubber soft more quickly, both with respect to the time and the energy consumed, than does cold mastication. In view of the fact that I was not so clear in the manner of expressing myself as the facts required, these statements may give rise to misunderstandings, and therefore I feel that I should explain this point in more detail. I meant to imply nothing more than that the rubber which was masticated on rolls at a temperature of 65° C., and which was also tested at this temperature, showed higher plasticity values than did rubber which was masticated and tested at 18° C. In spite of this, Dillon and Johnston, in checking this experiment, milled rubber at 73° and 112° C. and made their measurements in each case at 100° C.

To explain the phenomenon of mastication, it is indispensable to consider the idea of nerve and plasticity, terms which I have repeatedly defined in my publications. According to my idea,⁴ there are two parallel processes during mastication on a mill: (1) a process involving first a rupture of the rubber micelles with destruction of the nerve, and (2) a warming of the rubber, accompanied by a mutual displacement of the micelles, without destruction of the nerve. Upon mastication on hot rolls, the second effect is naturally predominant, and a plastic but nervy product results. On the other hand, mastication on cold rolls gives a product which is likewise plastic, although it has lost its nerve to a great extent. In testing both of these products at the same temperature, *e. g.*, at 100° C., as was done by Dillon and Johnston, the nerve is a decisive factor in the rate of outflow, *i. e.*, the greater the extent to which the nerve is destroyed, the greater is the outflow.

On the contrary, in my experiments which were referred to above, the thermal effect plays the chief part. According to our earlier results³ this effect is very great, and an increase in temperature of 20° C. doubles the rate of outflow. The differences in the nerve play a smaller part in this case.

If for example the question arises in manufacturing, what rubber is extruded the more rapidly through a machine at a temperature of 100° C., the answer must be unconditionally rubber which has been masticated on cold rolls. If one asks, however, at what temperature should the mastication be carried out in order to accomplish this as quickly as possible in the interest of time and energy economy, then the answer is that hot mastication is preferable. The objection will be raised that only the first point of view plays any part in practice, since the second leads to products which are too little plastic for further working. Unfortunately it is customary even today to plasticize mixtures by destroying the nerve to a great extent beforehand, and in this way to partially destroy a property which makes rubber so valuable and which up to the present time is lacking in all synthetic products. Naturally I do not underrate the difficulties which are involved in solving the problem under discussion, but I consider it my duty to call attention to them once more, and I shall withhold any further details for a work which in shortly to appear.

In conclusion, I am glad to learn that Dillon and Johnston are likewise convinced that a plastometer of the Marzetti type is better adapted to the total plasticity range in rubber than is a parallel-plate plastometer.

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- ³ Bachmann, Behre, and Blankenstein, *Kolloid-Z.*, **57**, 64 (1931).
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The Tensile Properties of Latex Products

Harry Barron

The rubber manufacturer of today is brought up in the tradition of facts and figures. The one without the other is useless. There can be no doubt that much of the present prosperity of the rubber industry is due to widespread benefits conferred by the publication of research work on rubber, and the standardization of production. The major discoveries in the recent history of rubber, such as the discovery of accelerators, the discovery of reinforcing action, and more recently the rediscovery of latex, have invariably followed a similar trend. The first activities in each case have been purely of a qualitative nature. After the frenzied rush to patent discoveries has subsided, everybody has settled down to find out the quantitative effects of the respective products when incorporated into rubber, subjected to the various rigorous processes normally employed. Careful research work has brought its reward, in so far as the scope of the respective products has widened, quality has improved, and costs have been very much reduced. In every case progress has been made on all sides, physical, chemical, and technical. In this respect latex is lopsided.

It is a remarkable fact that at the present time, when latex appears to be more and more widely employed, manufacturers are not at all enthusiastic about it. They certainly are not falling over themselves to apply it. This is a matter that warrants investigation.

Quantitative Information about Latex Is Lacking

When a manufacturer is faced with a new ingredient or raw material he asks several questions, among which are: (1) is it cheap, (2) does it process easily, (3) is new plant necessary, (4) is the finished product improved, (5) what does it do chemically, (6) what does it do physically, and so on? Any commercial compounding ingredient, be it accelerator, filler, pigment, etc., will have ample information on each and every point well documented with facts and figures. Unfortunately, the same cannot be said of latex, which is befogged with vague claims that are unsubstantiated. It is true that there are certain difficulties associated with latex: it requires careful handling; the patent question is so involved; there are certain inherent defects associated with its use. But these are not hard to overcome. On the other hand, where are the figures for tensile strength of latex mixings, what elongations are possible, how does it age, how does it vulcanize? In other words, what is its behavior in terms which will be comprehensible to the rubber manufacturer, and will influence him to take an interest in its possibilities?

Everywhere, in connection with products obtained from latex and in latex work, there is met the statement that the product obtained is superior in tensile properties to that obtained from masticated rubber, and has far better resistance to aging. From the scanty data to be found in the literature of the subject it must be accepted that these opinions are empirical, and not based on comprehensive tests. It is of some interest to examine the existing information on the subject.

Schidrowitz (*Trans. Inst. Rubber Ind.*, 1, 272 (1925)), as in most work connected with rubber, appears to be foremost with figures. In connection with vulcanized latex, he obtained tensile values which showed up the excellent qualities of latex rubber obtained from "Vultex" compared with cut and spread sheet:

	Vultex	Cut and Spread Sheet
TB	3200-4000 lb. per sq. in.	1530-2500 lb. per sq. in.
EB	9.7-10.2	8.3-11.1
Slope	34-36	36-45

ACCELERATED HEAT AGING

35 hours	Excellent condition	Considerable deterioration
70 hours	Excellent condition, 2000 lb. per sq. in.	Poor, 1000 lb. per sq. in.

NATURAL AGING AND LIGHT

20 days	Slight deterioration, 2450-3150	Poor
35 days	Fair commercial condition	Rotten

It must be accepted that these figures were obtained in a manner which made them comparable.

According to Beal (*Ind. Eng. Chem.*, 25, 609 (1933)), anode rubber has extraordinary strength and durability. Tensile and elongation data, such as 5900 lb. per sq. in. at 970 per cent and 6700 lb. per sq. in. at 925 per cent, are characteristic of anode compounds, but difficult to obtain with masticated rubber. Remarkably high tear resistances are shown. Good resistance towards abrasion and corrosive chemicals is another feature of anode rubber.

Davey (*J. Soc. Chem. Ind.*, 45, 1364 (1926)) carried out very interesting work, employing sprayed latex. He made up a mix of rubber 100, sulfur 8, glue 7, which he sprayed, dried, and molded. He compared the results with those obtained from similar experiments where the mix had been masticated.

TIME OF CURE (Min. at 141° C.)	75		90		105	
	Latex	Mast.	Latex	Mast.	Latex	Mast.
TB, lb. per sq. in.	2938	2290	2852	2606	2304	2204
EB, %	1029	941	1001	912	894	870
Combined S, %	4.30	4.79	4.86	5.50	5.61	6.09
E, 0.3 kg. per sq. cm. (432)	520	506	482	448	425	424
E, 0.6 kg. per sq. cm. (864)	694	644	671	594	615	573
E, 1.04 kg. per sq. cm. (1500)	798	754	777	705	721	691

Carrington (*Trans. Inst. Rubber Ind.*, 6, 450 (1931)) claimed that "Revultex" films gave an average tensile strength of 4800 lb. per sq. in. at 875 per cent elongation.

One of the most valuable contributions to the subject is the work carried out by the Dunlop chemists on latex thread, as outlined by Murphy (*Trans. Inst. Rubber Ind.*, 8, 339 (1932)). They showed that unvulcanized dry threads of latex have a tensile strength of 1000 lb. per sq. in. It must be remembered that values will be slightly higher than usual, owing to the threads being so much thinner than the standard test piece, a characteristic conducive to higher values. Some of the figures obtained are shown.

	Square Cut Thread	Latex Round	Latex Round
	90	80/90	90/100
TB, lb. per sq. in.	3200	5700	5640
EB, %	900	950	950
	Square Cut White	Square Cut Brown	Latex Round
	36/40	40	36/40
TB, lb. per sq. in.	3000	2350	4700
Pull in oz. to give—			
E = 200%	1.3	0.95	1.8
E = 400%	2.4	1.6	3.2
	Square Cut White	Latex Round	
	40	40/46	
TB, oz.	29.5	37.0	
E = 200%	1.3	1.3	
E = 400%	2.4	2.9	

Frequent tests showed that the resistance of latex thread to heat and light was exceptionally good.

Spear (*India Rubber World*, Nov., 1930, p. 73) claimed that Vultex gave tensile values up to 5000 lb. per sq. in., whereas ordinary latex only gave tensiles up to 1800 lb. per sq. in.

Rossman (*India Rubber World*, Oct., 1930, p. 67) stated that dipped latex gloves have aging, tearing, and wear resistance properties much superior to ordinary dipped gloves. They are also claimed to have a higher degree of toughness, pliability, and resistance to water and corrosive liquids. Typical tensile figures are 4090 lb. per sq. in., which after 96 hours in the oxygen bomb dropped to 3240 lb. per sq. in. Ordinary gloves show tensiles ranging from 1410–3210 lb. per sq. in., which, after similar aging, in some cases drop to zero, while the better ones drop from 1560–2460 lb. per sq. in.

Official credence was given to the superiority of latex products by the U. S. Bureau of Standards C:S. 41–32. The following specifications were recommended for latex and ordinary surgeon's gloves.

	Ordinary Gloves	Latex Gloves
Tb, lb. per sq. in.	2700	3500
EB, %	600	820
Tb after 5 sterilizations at 15 lb. for 15 min.	1500	2500
Tb after 10 sterilizations as above	Not specified	2000
Geer oven at 70° C.		
7 days	Not specified	3000 lb. per sq. in.
14 days	Not specified	2500 lb. per sq. in.
21 days	Not specified	2000 lb. per sq. in.

With the object of making a start in the direction already suggested, experiments have been carried out to determine whether these high tensile values for latex products could be reproduced systematically.

Experimental Work

(a) *Latex.*

The following mix was made up:

Rubber	100	(60% latex) parts
"Z. P. D."	0.5	part
2-Mercaptobenzothiazole	0.2	part
Sulfur	2.0	parts
Zinc oxide	1.0	part
Casein	1.0	(10% soln.) part

This was allowed to stand for several days, was stirred daily, and was then decanted from residual deposits.

It was poured into a series of shallow glass trays to a depth of 3 millimeters and allowed to dry for 7 days at 20° C., forming after that time a continuous film about 2 millimeters thick. These sheets were then cured in hot air for 20 minutes at 120° C.

Rings were cut from the sheets, and tested on the Schopper machine in the usual manner. Curves were then drawn connecting elongation with stress.

Simultaneously a similar series of experiments was carried out with 60% Vultex and curves drawn from the results obtained. Of course, in this case vulcanization was unnecessary.

(b) *Rubber.*

Rubber mixes were made up as follows:

Rubber 100	
S	2.0 parts
2-Mercaptobenzothiazole	0.2 part
"Z. P. D."	0.5 part
Casein	1.0 part

Vulcanized—15 min. at 120° C.

Rubber 100	
S	2.0 parts
2-Mercaptobenzothiazole	0.2 part
"Z. P. D."	0.6 part
Casein	1.0 part
Gas black	35.0 parts

Vulcanized—15 min. at 120° C.

Test rings were cut from these and broken on the Schopper machine. The values obtained are shown in Table I and plotted in Fig. 1.

It will be seen that the tensile strengths at break of the latex samples do not differ very much from the tensile strength of a strongly reinforced carbon black, though the elongations differ greatly.

The resilient energy, which is generally regarded as the criterion of reinforcement, was next measured planimetrically, being represented by the area between the stress strain curve and the elongation axis (see Barron and Cotton, *Trans. Inst. Rubber Ind.*, 7, 209 (1931)).

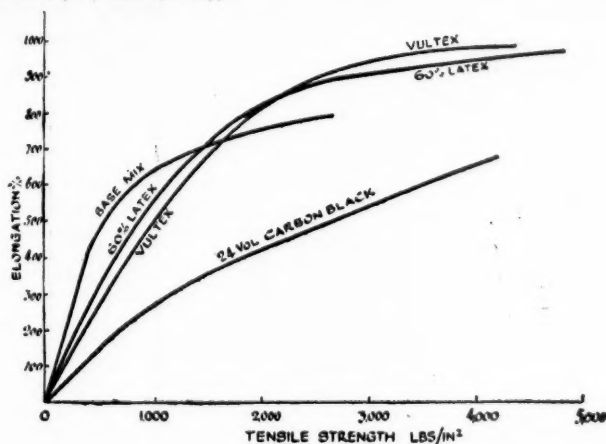


Figure 1

TABLE I

Elongation Per Cent	Base Mix, Lb. per Sq. In.	60 Per Cent Latex Compounded, Lb. per Sq. In.	60 Per Cent Vultex Lb. per Sq. In.	Carbon Black 24 Vols., Lb. per Sq. In.
0				
100		327	398	681
200		480	597	1196
300	327	628	753	1865
400	397	795	1006	2890
500	597	1080	1278	3484
600	795	1506	1597	4269
700	1494	1906	1996	(660) Eb
800	2703 (790) Eb			
900		2928	2648	
1000		4880 (960) Eb	4383 (970) Eb	
Resilient energy, ft. lbs. per cu. in.	393	738	735	726

Discussion

It has been established that the tensile strength of vulcanized rubbers obtained directly from latex is much higher than the values obtained from vulcanized

rubbers of similar composition, but in which the rubber has been masticated. Elongations observe the same trend. The remarkable result, however, is that latex rubbers have extraordinarily high energy contents, which according to present-day conceptions represent high reinforcement.

One of the chief objects of compounding has been to reinforce vulcanized rubber. Yet experimental evidence shows that the energy existing in a vulcanized latex rubber is in excess of the total energy content of even the most highly reinforced rubber compounds. The energy changes represented in the transition from latex to compounded reinforced rubber is illustrated in Fig. 2.

Reinforcing fillers will not exert any reinforcing action when added to latex, even when they are colloidal, the reason being that there is no actual contact between the rubber globule, which tenaciously retains its individuality, and the filler, a condition which appears to be fundamentally necessary for any form of reinforcement. According to Twiss (*Trans. Inst. Rubber Ind.*, 6, 419 (1931)), carbon black, though evenly dispersed in latex, gives a product showing no signs of reinforcement, and having very poor tensile properties. Yet the slightest

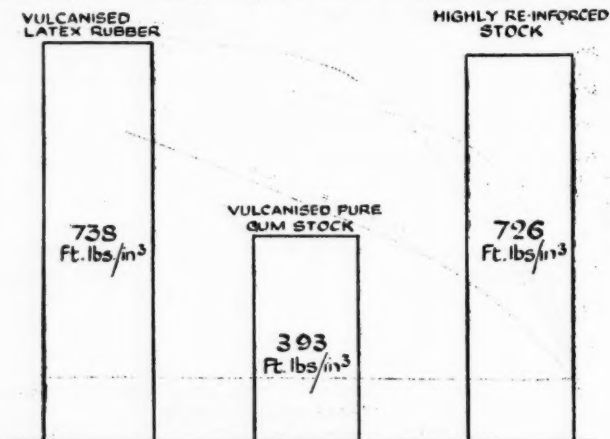


Figure 2—Comparative Energy Contents

mastication of the coagulum causes reinforcement to show up. On the other hand, ingredients necessary for vulcanization, such as sulfur, accelerators, and small quantities of zinc oxide, when in the colloidal condition, effectively manage to perform their normal functions.

It is well established that the individual globules existing in the latex are delineated in the dried product, both when unvulcanized or vulcanized (see Park and Sebrell, *Ind. Eng. Chem.*, 17, 1173 (1925)), and Schidrowitz (*India Rubber World*, 20, 6 (1909)). The drying out of a latex film, according to the ideas expressed by the author (*Rubber Age* (London), 15 (1934)), explain the retention of this individual structure. It is a fact that the existence of any particles in a latex film weakens it, particularly affecting the tear resistance. Therefore, it would appear that the great tensile strength and resilient energy shown by latex rubber is vested in the continuity of that reticular structure. The presence of any fillers weakens the structure, as also do gas bubbles.

It is interesting to note that Fisher, according to Schidrowitz (*India Rubber Journal*, 82, 693 (1931)), stated that slabs of rubber permitted to vulcanize embedded in sulfur, at ordinary temperature, after 384 days showed tensile strength

of 4160 lb. per sq. in. and combined sulfur of 2.93 per cent. The tensile strength is remarkably high for a masticated pure gum mix, and comes into the realm of values obtained from latex.

The inference which links this experiment with the conditions pertaining to latex is, that the rubber is in a position where it can take up as *little* sulfur as is required for vulcanization.

The theoretical implications involved in the results obtained in this investigation are reserved for a future communication.

Rubber from Latex Coagulated with Sulfuric Acid

G. Martin and W. S. Davey

STAFF OF THE LONDON ADVISORY COMMITTEE FOR RUBBER RESEARCH (CEYLON AND MALAYA)

An article by Wiltshire in the *Journal of the Rubber Research Institute*, November, 1932, p. 94, on the use of sulfuric acid as a coagulant of latex has attracted considerable attention among rubber manufacturers who have expressed some alarm at the possibility of the extended use of this chemical for coagulation. The India Rubber Manufacturers' Association, Great Britain, stated that "it was felt that it is highly undesirable that such a practice should be adopted without first ascertaining that recognized standards of performance, including aging, will be maintained in the finished manufactured articles."

In view of the apprehensions of manufacturers, samples were supplied by the Rubber Research Institute to the London Advisory Committee in order to investigate as fully as possible the effect on the properties of the rubber of using sulfuric acid as a coagulant.

The samples comprised (a) two samples of smoked sheet coagulated with sulfuric acid and formic acid, prepared on a Malayan estate which regularly uses sulfuric acid as a coagulant; and (b) four samples of air-dried sheet prepared by the staff of the Rubber Research Institute. The air-dried sheet samples were in two pairs, and were prepared on different days, using acetic acid sheet as a control in each case. The sulfuric acid sample in the first pair was prepared using more acid than is usual on estates. Subsequently a further sample of air-dried sheet coagulated with sulfuric acid and prepared on the above Malayan estate was received for comparison with the smoked sheet samples from the same estate.

Particulars of the preparation of these samples are shown in Table I.

All the air-dried sheet samples showed signs of mold, particularly C, E, and F.

The samples were divided into two portions, one of which was submitted to tests by the India Rubber Manufacturers' Association and the other to the following tests by the staff of the London Advisory Committee:

Chemical Analysis	Determination of water-soluble sulfate present
Plasticity	Hardness (D_{10}) and mastication
Rubber-sulfur mix	(a) Vulcanization in 100:10 rubber-sulfur mix
	(b) Aging in 90:10 rubber-sulfur mix
Accelerator mix	(a) Vulcanization and aging in mercaptobenzothiazole mix
	(b) Vulcanization and aging in diphenylguanidine mix

The purpose of the chemical test is to indicate whether appreciable amounts of free sulfuric acid remain in the rubber after the coagulum has been machined, with the consequent removal of a considerable proportion of the non-rubber serum substances and probably also of the sulfuric acid coagulant.

The purpose of the plasticity tests is to indicate whether the use of sulfuric acid affects the manipulation of the rubber by manufacturers.

Vulcanization and aging tests were carried out in three mixings. The rubber-sulfur mixing was selected as one because it gives results which are very sensitive to abnormality in the non-rubber accessory substances and to deterioration of the

TABLE I

Sample	Where Prepared	Type of Sheet	Coagulant	Amount of Coagulant	D. R. C. of Latex Lb./Gal.	Other Details
A	A Malayan estate	Smoked	Formic acid	1 fluid oz. to 14.7 lbs. of rubber	1 $\frac{1}{2}$	9 days smoking
B	A Malayan estate	Smoked	Sulfuric acid	1 fluid oz. to 25 lbs. of rubber	1 $\frac{1}{2}$	9 days smoking
C	R. R. I.	Air-dried	Acetic acid	2.8grams per lb. of rubber	1 $\frac{1}{2}$	Soaked in water 1 hour after machining. Dried 2 $\frac{1}{2}$ days at 110-120° F
D	R. R. I.	Air-dried	Sulfuric acid	3.0grams per lb. of rubber	1 $\frac{1}{2}$	"
E	R. R. I.	Air-dried	Acetic acid	2.8grams per lb. of rubber	1 $\frac{1}{2}$	"
F	R. R. I.	Air-dried	Sulfuric acid	2.3grams per lb. of rubber	1 $\frac{1}{2}$	"
G	The same estate as samples A and B	Air-dried	Sulfuric acid	1 fluid oz. to 25 lbs. of rubber		

rubber hydrocarbon. The two accelerator mixings selected are more in accord with manufacturing conditions than the rubber-sulfur mixing. Both accelerators are popular, one representing an acidic and the other a basic type of accelerator. They may therefore react differently to traces of sulfuric acid in the rubber. They also differ in that one has antioxidant properties, and the other is without effect in this direction. The proportions of the different ingredients in each mixing were selected so as not to hide variability in different samples of rubber and are also in accord with manufacturing practice.

The investigation is considered to be fairly comprehensive from a laboratory point of view, though it does not cover all the points on which manufacturers would possibly like some assurance before approving the extended use of correct proportions of sulfuric acid as a latex coagulant. It is a reasonable presumption, however, that, if the rubber satisfies all these tests, there is only a remote chance that it will cause difficulty in the rubber factory or shorten the life of the finished article.

Chemical Examination

Each sample was extracted (Soxhlet extractor) with boiling water for two days, and the extract examined for acidity and soluble sulfate in the usual manner, with the result shown in Table II:

TABLE II

Sample	Coagulant	Acidity in Terms of Mg. of KOH per 100 G. Rubber	Soluble Sulfate (SO ₄) Per Cent
A	Formic Acid	13.6	0.007
B	Sulfuric "	22.4	0.020
C	Acetic "	4.8	Nil
D	Sulfuric "	5.6	Trace
E	Acetic "	6.4	Nil
F	Sulfuric "	Trace	Nil

The acidity of the aqueous extract of the estate samples is much higher than that of the samples prepared by the Rubber Research Institute. The latter were soaked in water after machining the coagulum to sheet and it is possible that the estate samples did not receive this treatment, which would undoubtedly remove some of the water-soluble material remaining in the rubber.

The amount of free sulfuric acid in the samples prepared by the Rubber Research Institute was so small that it could hardly be detected. There was more soluble sulfate in the estate sample coagulated with formic acid, and still more in that coagulated with sulfuric acid. The maximum amount of soluble sulfate in any of the samples was 0.02 per cent, which is no more than might be incorporated with rubber by manufacturers due to the use of slightly acid sulfur or zinc oxide.

These results indicate that the amount of free sulfuric acid remaining in the dry rubber after coagulation with sulfuric acid is not sufficiently large to alarm manufacturers, particularly if the coagulum is soaked in water after machining. It is possible to use excess of sulfuric acid for coagulation, and only a trace may be apparent in the dry rubber after machining and soaking the coagulum.

Plasticity

The results of plasticity tests are given in Table III.

TABLE III

Sample	Coagulant	D ₉₀ (Mm.)	Mastication No.
A	Formic	1.56	104
B	Sulfuric	1.49	108
C	Acetic	1.51	110
D	Sulfuric	1.42	97
E	Acetic	1.51	113
F	Sulfuric	1.42	100

Samples prepared with sulfuric acid are, in general, slightly softer than the control samples and masticate on the whole more easily. It appears likely therefore that the use of sulfuric acid will have an advantageous effect as regards the manipulation of rubber by manufacturers.

Vulcanization and Aging

The results of vulcanization and aging tests are shown in the Tables IV to VIII.

Table IV	Series of cures in rubber-sulfur mix 100:10.
Table V	Aging tests in vulcanized rubber-sulfur mix 90:10.
Table VI	Range of cures in a mercaptobenzothiazole mix.
Table VII	Aging tests in a mercaptobenzothiazole mix.
Table VIII	Aging tests in a diphenylguanidine mix.

There is no evidence that the sulfuric acid samples are weaker than the controls on vulcanization in the rubber-sulfur or accelerator mixings. In all the mixings the sulfuric acid samples on aging retain their strength for approximately the same period as controls. In some cases the controls are a little better than the sulfuric acid samples and in others the latter have the advantage.

The sulfuric acid coagulated air-dried sheets prepared at the Rubber Research Institute required approximately 14 per cent longer vulcanization than the controls in rubber-sulfur mixings, but the rate of vulcanization of the smoked sheet and air-dried sheet prepared on a Malayan estate is hardly affected by the use of sulfuric acid. The latter results are contrary to general experience, and in a number of cases it has been observed that the estate samples differ in their relative behavior

TABLE IV
Mixing: Rubber ... 100
Sulfur ... 10

Sample	Tensile Strength (lb. per Sq. In.) after Vulcanization at 148° C.				Elongation, Per Cent at Load of 1.04 Kg. per Sq. Min. after Vulcanization at 148° C.				Calculated Correct Time of Cure, t _{ca} , to Give Elongation 800 (Min.)
	120 Min.	140 Min.	160 Min.	180 Min.	120 Min.	140 Min.	160 Min.	180 Min.	
A. Smoked sheet, Formic acid	1960	2130	883	797	139.
B. Smoked sheet, Sulfuric acid	1850	2250	889	789	138
C. Air-dried sheet, Acetic acid	1910	2330	870	794	138.
D. Air-dried sheet, Sulfuric acid	1180	2140	2340	...	930	853	800	...	160.
E. Air-dried sheet, Acetic acid	1740	1950	893	810	142
F. Air-dried sheet, Sulfuric acid	1230	1710	2350	...	915	843	792	...	158
G. Air-dried sheet, Sulfuric acid	2400	2500	840	766	131

TABLE V
Mixing: Rubber 90
Sulfur 10

Sample	Time of Vulcanisation at 149° C. (Min.)	Tensile Strength (Lb. per Sq. In.) after Aging at 70° C. for Hours					Elongation (Per Cent) at Load of 1.04 Kg. per Sq. Mm. after Aging at 70° C. for Hours								
		0	48	96	120	144	168	192	0	48	96	120	144	168	192
A Smoked sheet Formic acid	106	1890	2520	2250	2100	1730	1930	1650	857	774	738	722	706	695	677
B Smoked sheet.	106	1880	2560	2020	2160	1850	1600	1280	864	782	748	720	708	692	...
C Sulfuric acid Air-dried sheet Acetic acid	107	1830	2130	1740	1490	360	874	780	729	710
D Air-dried sheet Sulfuric acid	125	1990	2210	1920	1860	1550	888	796	748	724	725
E Air-dried sheet Acetic acid	115	2030	2530	2100	2070	460	853	762	706	692
F Air-dried sheet Sulfuric acid	125	1900	2130	1830	1460	250	875	783	731	712

TABLE VI

Sample	Mixing:		Tensile Strength after Vulcanization at 126° C. for		Elongation at Load of 1.04 Kg. per Sq. Mm. after	
	Rubber		Vulcanization at 126° C. for		Vulcanization at 126° C. for	
	40 Min.	60 Min.	20 Min.	40 Min.	20 Min.	40 Min.
A Formic acid	1180	1830	2320	2410	2280	741
B Smoked sheet					...	744
Sulfuric acid	1000	2030	2030	2540	2360	746
C Smoked sheet					...	783
Acetic acid	1120	1590	2050	2280	2310	784
D Sulfuric acid	1280	2090	2430	2570	2390	761
Air-dried sheet					...	810
Acetic acid	730	1770	2080	2080	2160	807
Sulfuric acid	240	1430	1920	2120	2330	847
G Air-dried sheet	1200	2210	2300	2350	2360	763

Mixing: Rubber 100
 Zinc oxide 6
 Sulfur 3.5
 Stearic acid 1
 Mercaptobenzothiazole 0.5

TABLE VII

Sample	Time of Vulcanisation at 126° C. (Min.)	Tensile Strength (Lb. per Sq. In.) after Aging at					Elongation (Per Cent) at Load of 1.04 Kg. per Sq. Mm.							
		82.5° C. for Days					after Aging at 82.5° C. for Days							
		0	2	4	6	8	0	2	4	6	8	10	12	
A Formic acid Smoked sheet	80	2290	2770	2480	1840	500*	960	230	736	629	616	575
B Sulfuric acid Smoked sheet	80	2650	2330	2770	2330	1990	1560	740	734	664	642	613	574	560
C Acetic acid Air-dried sheet	80	2430	2770	2340	2150	1630	1520	750	771	663	651	623	587	563
D Sulfuric acid Air-dried sheet	80	2320	2550	2030	2340	850	890	200	721	660	653	619
E Acetic acid Air-dried sheet	80	2120	2570	2430	1930	1810	1370	710	775	690	681	644	626	603
F Sulfuric acid Air-dried sheet	100	2220	2140	2100	1690	1190	710	190	776	725	719	683
G Sulfuric acid Air-dried sheet	80	2650	2500	2200	1560	390	235	250	731	644	633	596

*Probably two exceptionally weak rings.

*Probably two exceptionally weak rings.

TABLE VIII

Sample	Time of Cure at 141° C. (Min.)	Tensile Strength (Lb. per Sq. In.) after Aging at 82.5° C. for Days							Elongation (Per Cent) at Load of 1.04 Kg. per Sq. Mm. after Aging at 82.5° C. for Days						
		0	2	4	5	6	7	7	0	2	4	5	6	7	7
		Mixing: Rubber 100 Zinc oxide 6 Sulfur 2.75 Diphenylguanidine 0.4													
A Formic acid	60	2050	2500	1500	1060	510	260	787	744	777
B Smoked sheet	60	2580	2400	1550	1450	1000	200	752	718	740	740
C Sulfuric acid	60	2450	1640	1200	1110	250	170	735	694	730
D Acetic acid	60	2160	2270	1460	1400	915	430	770	735	764	774
E Air-dried sheet	60	1980	2120	1250	1180	740	340	774	723	753
F Sulfuric acid	60	2370	2200	1160	660	160	170	795	762	780

from those prepared at the Rubber Research Institute. It is possible that the estate samples are abnormal, and that definite conclusions should be confined to those drawn from the results given by the Rubber Research Institute samples.

In the mercaptobenzothiazole mixing there is little difference between the estate samples, but the two pairs of air-dried sheets from the Rubber Research Institute show small differences which are in opposite directions.

In the diphenylguanidine mixing the air-dried sulfuric acid sheets prepared at the Rubber Research Institute give a softer vulcanizate than the controls, but the estate smoked sheet displays the opposite effect.

In the mercaptobenzothiazole mixing the sulfuric acid samples display a smaller increase in modulus during aging than the other samples. This is an advantage but it is not important, and is not displayed in the other mixings.

It appears from these results that the most important effect of the use of sulfuric acid is an alteration in rate of vulcanization, particularly in the rubber-sulfur mixing, and it is evident that the use of sulfuric acid on some estates and of acetic and formic on other estates must tend to increase variability and thereby prejudice manufacturers against the use of first-grade rubber.

The effect of the sulfuric acid when used in correct proportion is very small, however, when compared with the total variability which already exists. The rubber from some estates using formic or acetic acid as a coagulant may vulcanize twice as fast as that from others using the same coagulant, whereas the retardation of vulcanization owing to the use of sulfuric acid is less than 20 per cent, and may in some cases be much less.

In the case of accelerator mixings, the effect of using sulfuric acid cannot be measured in terms of rate of vulcanization, owing to the slow alteration in physical properties with period of vulcanization, but the limited data available indicate that the use of sulfuric acid would lead to an increase in variability which is small compared with that already existing in rubber from different estates.

The India Rubber Manufacturers' Association arrived at similar conclusions from the results of their tests on portions of the samples. Their report is as follows:

"With regard to the rubber coagulated with sulfuric acid it was found that, in every case, the rubbers so coagulated were slower curing than the standard rubbers in pure rubber stocks not containing added accelerator. When adjustment was made for this slowing-up in curing, the ultimate physical properties of the above were satisfactory.

"When stocks were used containing accelerators, different results were obtained depending on the choice of the accelerator. With an accelerator of the type of mercaptobenzothiazole, increased activation was obtained in the case of rubbers coagulated with sulfuric acid, while in the case of accelerators such as diphenylguanidine, where best results obtained with alkaline conditions, retardation was again found.

"It was again found that when these factors were recognized and the articles cured to an equivalent state of cure, similar aging properties were obtained. It would therefore, appear from the tests carried out that coagulation with sulfuric acid under properly controlled conditions could give rubbers with intrinsic properties equal to those obtained with standard methods of preparation. Our tests, however, do suggest that a rubber manufacturer who unwittingly received a substantial part of his deliveries in the form of rubber coagulated with sulfuric acid might encounter definite manufacturing trouble due to the rate of vulcanization being abnormal, and due to the fact that variable results would obtain according to the type of accelerator being used and the type of article being manufactured.

"We think that you will realize that owing to the small size of the samples sent, only laboratory tests could be carried out, and it was not possible to make a variety of manufactured articles which could be put to service tests. The tests, however, do serve to show that the use of sulfuric acid requires very careful consideration on the part of rubber growing interests, and they do definitely indicate the possibility of normal manufacture being thrown out of gear due to the properties of the sulfuric acid-coagulated rubber being abnormal with regard to cure.

"We therefore advise that rubber coagulated with sulfuric acid should not be put on the market without the method of coagulation being definitely stated."

Summary

The results of tests carried out in the laboratories of the London Advisory Committee show that when sheet rubber is prepared by coagulation of latex with sulfuric acid:

- (1) Only a trace of free sulfuric acid remains in the dry rubber.
- (2) The rubber is somewhat easier to manipulate in rubber manufacturing operations than that prepared by coagulating latex with acetic acid.
- (3) The rubber has satisfactory mechanical properties when vulcanized in rubber-sulfur or accelerator mixings.
- (4) The rubber ages satisfactorily in rubber-sulfur and accelerator mixings.
- (5) The use of sulfuric acid would tend to increase the variability in vulcanization of first-grade rubber unless its use became general.

Conclusions

The use of correct proportions of sulfuric acid as a coagulant is not harmful to the intrinsic properties of the rubber. On the other hand, the economy due to its use is not large, and there is a possibility of harm arising in two directions, *viz.*:

(1) As long as it is used by only a proportion of estates it will increase slightly the variability of rubber and so tend to prejudice all manufacturers against first-grade rubber in favor of lower grades in which a high degree of uniformity cannot reasonably be expected. There is no doubt that some manufacturers view with apprehension the possibility of an increase, however slight, in the variability of first-grade rubber. In addition, manufacturers of high-grade special articles would be unwilling to use on a large scale rubber which they knew had been coagulated with sulfuric acid unless they first had an opportunity of making prolonged and thorough tests with their own products.

(2) The accidental use of excess of sulfuric acid, in addition to causing difficulty on an estate, is known to have a definitely harmful effect on the rubber. The use of excess of acetic or formic acid has no serious effect on the properties of the rubber.

It is not anticipated that the plantation industry would suffer serious disadvantage from the general use of sulfuric acid as a coagulant, but the economy does not appear to be sufficient to justify the risk, especially in view of the objections raised by manufacturers.

The Specific Gravity of Preserved Latex

Edgar Rhodes

RUBBER RESEARCH INSTITUTE OF MALAYA, KUALA LUMPUR

Introduction

The literature on latex contains a number of references to the specific gravity of fresh latex, but published information on the specific gravity of preserved latex in the condition in which it reaches the consumer appears to be practically non-existent. de Vries^{1,2} and Scholtz and Klotz³ investigated the specific gravity of undiluted fresh latices of various dry rubber contents, and from their results each deduced the specific gravity of the disperse or rubber phase. The average specific gravity of the rubber globule as deduced by de Vries is 0.914. Scholtz and Klotz's value for the disperse phase is 0.901, which is appreciably lower than that of de Vries.

Although the published literature contains no references to the specific gravity of commercial preserved latex, the Rubber Trade Association of London gives a table of values in its latex contract forms, but details are lacking as to the total number of experimental observations which the table represents. A significant feature is that, by extrapolation of the dry rubber content values to 100 per cent, after the manner of Scholtz and Klotz, the figures obtained for the specific gravity of the rubber disperse phase is 0.912, which agrees fairly well with that of de Vries for fresh latex, and which is considerably higher than that of Scholtz and Klotz.

In view of the paucity of information available on the specific gravity of preserved latex, it seemed desirable to obtain additional data and incidentally to make a further check on the published values for the specific gravity of the rubber disperse phase.

The primary object was to construct, after the manner of the Rubber Trade Association, a specific gravity table which might reasonably be said to be representative of average commercial preserved latex over a fairly wide range of dry rubber contents. de Vries and Scholtz and Klotz have both shown that, with fresh latices of any given dry rubber content, an appreciable variation in specific gravity is found. Seasonal variations in the amount of serum components and similar variations due to the nature and severity of the tapping system employed, together with accidental or deliberate dilution of latex with water in the field, combine to produce specific gravity variations in latices of the same dry rubber content. In working with preserved latex there is an additional variable, in the amount of ammonia present and in the form in which the ammonia is added. In attempting to prepare a table for average commercial preserved latices, it is obviously important therefore to examine a large number of samples from a reasonable number of different sources.

The findings of Scholtz and Klotz are based upon an examination of 85 samples, all of which were taken from the same estate source and a number of them from individual trees on the experimental area. In the present work individual tree samples have been rigidly excluded, the latex has been drawn from a number of different estates and the total number of samples examined is ten times that of Scholtz and Klotz.

SECTION A
Experimental

Sources of Latex.—In Table I below the various sources of latex are set out, while column 3 of Table II indicates the sources of the samples in various zones of dry rubber content.

TABLE I
SOURCES OF LATEX

Estate No.	District	Latex from
1	Negri Sembilan	Seedling trees
2	Selangor	Seedling trees
3	Selangor	Seedling trees
4	Selangor	Seedling trees and four clones
5	Selangor	Seedling trees
6	Johore	Seedling trees
7	Selangor	Seedling trees
8	Selangor	Seedling trees
9	Selangor	Seedling trees

The samples were collected as opportunity offered over a period of approximately six months, and the attempt was made to cover the approximate normal range of dry rubber contents, 28–50 per cent. It is unlikely that commercial preserved latex will ever be required at a dry rubber content less than 28 per cent, while the tree itself fixes the dry rubber content of 48–50 per cent as the richest latex which can be shipped in any quantity without artificial concentration. The majority of the samples having dry rubber contents in the range 28–32 per cent were obtained from an area on Estate No. 2, which is being tapped on a fairly drastic system as a preliminary to re-planting. On this estate the chances of deliberate dilution of latex by the tappers in the field were small and samples were not drawn for test on wet days. Latex of high dry rubber content, in the zone 46–50 per cent is difficult to obtain in quantity, and a large proportion of the samples in this zone were of necessity obtained from Estates Nos. 2 and 7, which happen to be two of the few Malayan estates which export unconcentrated latex of high dry rubber content.

Sampling and Preservation.—It was not possible, except in a few cases, to draw samples from daily bulks of latex from a whole estate or estate division, chiefly because the time required for the accumulation of a sufficiently large number of separate test samples would have been far too long. In order to make possible the collection of a suitable number of samples in a reasonable time, the yield from a tapper's task of 250–300 trees was taken as a suitable bulk from which a sample might be drawn. By this means it was possible to collect from any estate on a given day a number of samples, each of which represented the mixed product from a fair tree population. The adoption of this procedure introduced, in nearly all cases, the necessity of preservation with liquid rather than with gaseous ammonia. The addition of liquid ammonia as a preservative has the two-fold effect upon the specific gravity of slight aqueous dilution, together with a reduction due to the ammonia itself. The dilution effect is, however, by no means so great as the accidental or deliberate dilution which is very common in commercial practice, as, for instance, when rich latex of 42–43 per cent dry rubber content is deliberately diluted with water at the factory to 38–39 per cent before shipment, and the use of liquid ammonia in the preservation of the test samples is not therefore unwarranted. The permissible range of ammonia content was taken as 0.5–0.7 per cent, and any sample containing an amount of ammonia within this range was accepted for test.

Dry Rubber Content and Specific Gravity Determination.—Dry rubber contents were determined in duplicate on each sample after thorough shaking, by the method described by Bishop and Fullerton.⁴ Values for dry rubber content were thus obtained as weight percentages, or in other words as the weight of dry rubber contained in a given weight of latex.

Specific gravity determinations were also made in duplicate on each sample by the specific gravity bottle method, after very thoroughly shaking each sample to re-disperse settled solids. No temperature refinements were introduced. These were scarcely warranted by the very nature of the investigation and its uncontrollable variations. In any case, room temperature at the Institute is always very constant in the region 29–30° C.

Results

In all, 852 samples were examined for dry rubber content and specific gravity; the dry rubber content range covered was 28–50 per cent approximately. The results were then tabulated according to dry rubber content into groups of two units after the manner of the Rubber Trade Association in the presentation of its values. In this way, the total dry rubber content range was divided arbitrarily into eleven groups. The number of individual samples falling into each group naturally varied, the most populous group containing 117 individuals and the least populous 38 only. This unequal distribution was unavoidable. For each group of two dry rubber content units, the mean dry rubber content and the mean specific gravity were then calculated. Columns 1, 2, 4, and 5 of Table II present the values so obtained.

Analysis of Results

It was expected that the eleven values for mean specific gravity at the corresponding mean dry rubber content values, set out in columns 4 and 5 of Table II, would not lie exactly in a straight line and a mathematical analysis of the spread of the individual specific gravity values in each group, about the mean for that group, was made in order to determine the significance of each of the means. The standard deviation of the individual values from the mean was calculated for each group, together with the corresponding probable error. Similarly, the standard deviation and probable error of the mean itself were obtained; these are set out in columns 6, 7, 8, and 9 of Table II. In examining the values for the standard deviation and probable error of a single determination, it is seen that, even in the two worst groups, the chances are even that a single determination falls within ± 0.0015 of the corresponding mean specific gravities for these groups. The standard deviation of the means themselves about the true mean, which would result from an infinite number of determinations, is in the worst case ± 0.00032 , while in six of the eleven groups it is ± 0.00015 or less. Even in the worst case the chances are even that the arithmetic mean lies within ± 0.00022 of the true value, while in seven of the eleven groups the probable error does not exceed ± 0.00013 .

These calculations led to the broad conclusion that no great advantage could accrue from a multiplication of the already large number of observations and that, if the eleven values in columns 4 and 5 of Table II for mean dry rubber content and mean specific gravity were plotted, the most probable line through these points would have significance.

It is common in the preparation of a graph to plot the various points and to decide by simple visual inspection the position of the line or curve which best fits

TABLE II
SPECIFIC GRAVITY AND DRY RUBBER CONTENT FOR 852 SAMPLES OF PRESERVED LATEX

Group D. R. C. Per Cent by Weight	Total Samples in Group	Sources (See Table I)	Mean D. R. C. (<i>t</i>)	Mean Specific Gravity (<i>s</i>)	About the Arithmetic			Specific Gravity Distribution			About the Line		
					Standard Deviation <i>t</i>	Mean Probable Error $0.6745 \times t$	Standard Deviation of Arith. Mean <i>t</i>	Mean Probable Error of Arith. Mean $0.6745 \times t$	$s = -0.001158 t + 1.0177$ Standard Deviation <i>t</i>	Mean Probable Error $0.6745 \times t$	Standard Deviation <i>t</i>	Mean Probable Error $0.6745 \times t$	Standard Deviation <i>t</i>
1	2	3	4	5	6	7	8	9	10	11			
28.1-30.0	97	1, 2, 3	29.3	0.9831	± 0.0012	± 0.0008	± 0.00012	± 0.00008	± 0.0014	± 0.0009			
30.1-32.0	116	1, 2, 4	31.0	0.9820	± 0.0012	± 0.0008	± 0.00011	± 0.00008	± 0.0011	± 0.0008			
32.1-34.0	47	1, 2, 3, 4, 5	33.0	0.9796	± 0.0019	± 0.0013	± 0.00028	± 0.00019	± 0.0017	± 0.0012			
34.1-36.0	59	1, 2, 3, 4, 5	35.2	0.9773	± 0.0022	± 0.0015	± 0.00029	± 0.00019	± 0.0021	± 0.0014			
36.1-38.0	117	1, 2, 3	37.3	0.9744	± 0.0022	± 0.0015	± 0.00020	± 0.00013	± 0.0020	± 0.0013			
		4, 5, 6, 7, 8, 9											
38.1-40.0	102	1, 2, 3, 4, 5, 6, 7, 8, 9	39.1	0.9725	± 0.0015	± 0.0010	± 0.00015	± 0.00010	± 0.0014	± 0.0009			
		6, 7, 8, 9											
40.1-42.0	104	2, 4, 5, 6, 7	40.9	0.9706	± 0.0014	± 0.0009	± 0.00014	± 0.00010	± 0.0015	± 0.0010			
42.1-44.0	39	2, 4, 5, 6, 7	43.0	0.9682	± 0.0020	± 0.0014	± 0.00032	± 0.00022	± 0.0018	± 0.0012			
44.1-46.0	38	2, 4, 5, 6, 7	45.2	0.9650	± 0.0017	± 0.0011	± 0.00028	± 0.00019	± 0.0014	± 0.0009			
46.1-48.0	85	2, 4, 7	47.1	0.9626	± 0.0012	± 0.0008	± 0.00013	± 0.00009	± 0.0012	± 0.0008			
48.1-50.0	48	2, 6, 7	48.8	0.9614	± 0.0009	± 0.0006	± 0.00013	± 0.00009	± 0.0010	± 0.0006			
	852										± 0.0015	± 0.0010	

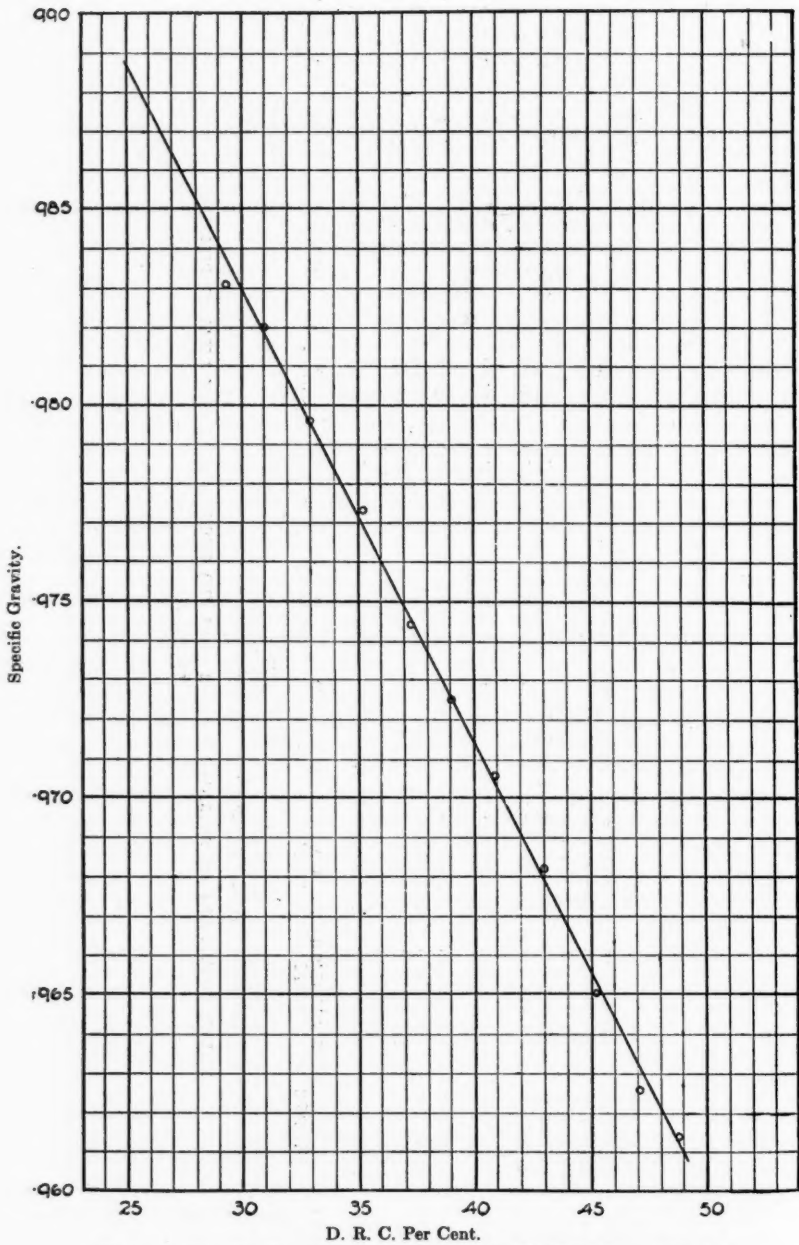


Figure 1—Specific Gravity and Dry Rubber Content of Preserved Latex

them. In the work of Scholtz and Klotz the position of the most probable line was decided by plotting each of the 85 individual experimental points and drawing a line by inspection more or less centrally through the rather widely scattered point mass. The line so obtained for a range of dry rubber contents of 28-56 per cent was then extrapolated in one direction to 100 per cent rubber, so that, in other words, the extrapolation zone in one direction was much greater than the experimental zone itself. A very slight error in the slope of the line in the experimental zone must lead to a considerably magnified error in the deduced value for the specific gravity of the rubber disperse phase. Extensive extrapolation can in any case be criticized on many grounds, but where, as in this case, it is unavoidable, it is obviously important to fix the position of the experimental line not by simple visual inspection and personal judgment, but by mathematical calculation. The criticism that the investigator might have chosen by inspection a slightly different but apparently equally satisfactory line through the experimental points, and so obtained a different value at the extrapolation limit, can only be avoided if the position of the most probable line is determined mathematically.

In the present work the 852 values had been reduced, by the initial grouping, to the eleven mean points set out in columns 4 and 5 of Table II, and it had been shown that each of the mean points had statistical significance. They lie nearly on a straight line (see Fig. 1) and, though the difficulty of fixing by inspection the line which best fits them is thereby rendered much less than in the case of Scholtz and Klotz, whose experimental points were ungrouped and therefore widely scattered, it was decided to calculate the position of the line which best satisfied the eleven points.

TABLE III

Mean D. R. C. (<i>t</i>)	(<i>t</i> ²)	Mean Specific Gravity (<i>s</i>)	(<i>st</i>)
29.3	858.49	0.9831	28.80483
31.0	961.00	0.9820	30.44200
33.0	1089.00	0.9796	32.32680
35.2	1239.04	0.9773	34.40096
37.3	1391.29	0.9744	36.34512
39.1	1528.81	0.9725	38.02475
40.9	1672.81	0.9706	39.69754
43.0	1849.00	0.9682	41.63260
45.2	2043.04	0.9650	43.61800
47.1	2218.41	0.9626	45.33846
48.8	2381.44	0.9614	46.91632
$\Sigma t = 429.9$	$\Sigma t^2 = 17,232.33$	$\Sigma s = 10.6967$	$\Sigma (st) = 417.54738$
$n = 11$			

The equation of the most probable line through the eleven mean points was calculated by the application of the "theorem of least squares" described by Feldman.⁵ It is required to calculate the most probable values of *m* and *b* in the equation

$$s = mt + b$$

where *s* = specific gravity and *t* = dry rubber content. The value for *m* is given by the equation

$$m = \frac{\Sigma t \times \Sigma s - n \Sigma (st)}{(\Sigma t)^2 - n \Sigma t^2}$$

and the value for *b* by

$$b = \frac{\sum t \times \sum (st) - \sum t^2 \times \sum s}{(\sum t)^2 - n \sum t^2}$$

where n = number of specific gravity-dry rubber content pairs.

Table III shows the arithmetical operations from which the values of m and b were derived by simple algebraical substitution in the above equations.

The values derived for m and b are as under:

$$\begin{aligned} m &= -0.001158 \\ b &= 1.0177 \end{aligned}$$

and the equation of the most probable specific gravity-dry rubber content line—is thus

$$s = -0.001158t + 1.0177$$

From this one may calculate the specific gravity s for any known dry rubber content t , and by calculating the specific gravity for each of the eleven dry rubber content means and comparing it with the experimental specific gravity mean itself, a picture is obtained of the closeness of approach of the experimental points to the line which represents them most fairly as a group. Table IV presents this comparison.

TABLE IV
CLOSENESS OF APPROACH OF THE GROUP-MEAN POINTS TO THE LINE $s = -0.001158t + 1.0177$

Mean D. R. C.	Mean S. G. Experimental	S. G. Calc.	Deviation from Experimental Group-Mean Specific Gravity
29.3	0.9831	0.9838	+0.0007
31.0	0.9820	0.9818	-0.0002
33.0	0.9796	0.9795	-0.0001
35.2	0.9773	0.9769	-0.0004
37.3	0.9744	0.9745	+0.0001
39.1	0.9725	0.9724	-0.0001
40.9	0.9706	0.9703	-0.0003
43.0	0.9682	0.9679	-0.0003
45.2	0.9650	0.9654	+0.0004
47.1	0.9626	0.9632	+0.0006
48.8	0.9614	0.9612	-0.0002

It is observed that, at nine of the eleven dry rubber content values, the closeness of the specific gravity group-mean to the value shown by the line itself is 0.0004 or less. In Fig. 1, this is demonstrated graphically.

It will be remembered that, in the initial mathematical treatment, standard deviations of specific gravity were calculated about the mean specific gravity for a group which covered two units of dry rubber content. Within that group the deviation of all individual specific gravities were computed from the mean specific gravity for that group without regard to the dry rubber content associated with the specific gravity of any particular individual in the group. The variation of specific gravity with dry rubber content within groups was not taken fully into account. It remained therefore to make certain that the dispersion of individual values within any group *about their own section of the chosen line* was not distinctly greater than that already derived about the single point which represents the group-mean specific gravity. It was necessary to compute the deviation of every

experimental specific gravity value within a group from the specific gravity indicated by the line at the exact dry rubber content of that sample. Specific gravities were calculated along the chosen line at intervals of 0.1 unit of dry rubber content over the whole experimental range. The individual experimental specific gravities within each group were then related to the calculated specific gravity at their respective dry rubber contents. In this way it was possible to derive values for the standard deviation of group members about the line rather than about the group-mean point. The data so obtained are presented in columns 10 and 11 of Table II. When these values are compared with the corresponding values, in columns 6 and 7, respectively, for standard deviation about the group means, it is seen that for seven of the eleven groups the dispersion about the line is slightly less than that about the corresponding group-mean; in one group the degree of dispersion is the same about the line and group-mean, and in the remaining three groups, the dispersion about the line is slightly greater than that about the corresponding group-mean. This indicates that, taking into account the dry rubber content of each of the experimental points, the grouping of their specific gravities is better about the chosen line than about the specific gravity group-means, upon which the line is based; the line $s = -0.001158t + 1.0177$ was therefore accepted as representing the relation between specific gravity and dry rubber content in preserved latex. By determining the standard deviation of the whole of the 852 samples from the line (see Table II, column 11, bottom) it may be concluded that, if a single sample only were available for test, the chances would be even that the specific gravity obtained would lie within ± 0.0010 of the value shown by the line at that dry rubber content.

It was now possible to prepare the desired table for specific gravity and dry rubber content, and this is presented as Table V. In order to check the values of de Vries^{1,2} and Scholtz and Klotz³ for the specific gravity of the rubber disperse phase, extrapolated values up to 100 per cent rubber content have been included in the table, and it is seen that the results lead to a specific gravity for the rubber disperse phase of 0.9019, which is in good agreement with and confirmatory of the value of 0.901 derived by Scholtz and Klotz for fresh latex. There is, therefore, some reason to believe that the value of 0.914 found by de Vries (*loc. cit.*), and the value of 0.912 derived by extrapolation from the Rubber Trade Association specific gravity table are high.

It has already been explained that all values for specific gravity and dry rubber content were determined on the various samples of preserved latex after thorough shaking to re-disperse insoluble heavy solids. It is also a fact that the values for dry rubber content were obtained of necessity by coagulation, and the weight of the dry coagulum was taken as representing the rubber disperse phase. It is obvious that a dry rubber content obtained in this way, while quite satisfactory for commercial purposes, does not give a coagulum consisting simply and solely of pure rubber hydrocarbon in the strictly scientific sense. It is well known that, when preserved latex is allowed to stand, an appreciable amount of heavy solids settles out, and it would be expected that the specific gravity of a latex from which the solids had been allowed to settle, would be less than that shown by the same latex after thorough shaking. Similarly, where preserved latex has been subjected to simple centrifugal clarification which removes solids, not only would it be expected that the specific gravity of the clarified latex would be less than that of the original latex, but also that, in carrying out a determination of dry rubber content, the coagulum obtained might be more free from adventitious heavy non-rubber solids and thus more closely represent pure rubber hydrocarbon. It follows

therefore that specific gravity-dry rubber content values for centrifugally clarified latex, and also for latex which has been concentrated centrifugally might be expected to lie a little below those for preserved latex, and to lead to a specific gravity for the rubber disperse phase itself, which might be slightly less than that derived

TABLE V
SPECIFIC GRAVITY TABLE FOR NORMAL PRESERVED LATEX
From the Line $s = -0.001158t + 1.0177$

D. R. C. (t)	S. G. (s)	Lb. per Gallon Water = 10	Oz.
0	1.0177
10	1.0061
15	1.0003
20	0.9945
25	0.9887	2	7 ¹ / ₂
26	0.9875	2	9
27	0.9864	2	10 ¹ / ₂
28	0.9853	2	12 ¹ / ₄
29	0.9841	2	13 ³ / ₄
30	0.9830	2	15 ¹ / ₄
31	0.9818	3	0 ³ / ₄
32	0.9806	3	2 ¹ / ₄
33	0.9795	3	3 ³ / ₄
34	0.9783	3	5 ¹ / ₄
35	0.9772	3	6 ³ / ₄
36	0.9760	3	8 ¹ / ₄
37	0.9749	3	9 ³ / ₄
38	0.9737	3	11 ¹ / ₂
39	0.9725	3	12 ³ / ₄
40	0.9714	3	14 ¹ / ₄
41	0.9702	3	15 ³ / ₄
42	0.9691	4	1
43	0.9679	4	2 ¹ / ₂
44	0.9667	4	4
45	0.9656	4	5 ¹ / ₂
46	0.9644	4	7
47	0.9633	4	8 ¹ / ₂
48	0.9621	4	10
49	0.9610	4	11 ¹ / ₄
50	0.9598	4	12 ³ / ₄
51	0.9586	4	14 ¹ / ₄
52	0.9575	4	15 ³ / ₄
53	0.9563	5	1
54	0.9552	5	2 ¹ / ₂
55	0.9540	5	4
56	0.9529	5	5 ¹ / ₄
57	0.9517	5	6 ³ / ₄
58	0.9505	5	8 ¹ / ₄
59	0.9494	5	9 ¹ / ₂
60	0.9482	5	11
61	0.9471	5	12 ¹ / ₂
62	0.9459	5	13 ³ / ₄
65	0.9424
70	0.9366
75	0.9308
80	0.9251
90	0.9135
100	0.9019

The figures in lighter type are obtained by extrapolation beyond the experimental zone.

from the examination of normal preserved latex. It was felt that, without entering upon a systematic study of centrifuged latices, a few observations might afford some additional confirmation of the indication that the values of 0.914 and 0.912 for the specific gravity of the rubber phase of latex are probably on the high side. Some additional experiments were therefore made and these are described in Section B which follows.

SECTION B

Experimental

Specific gravity variations in normal preserved latex after simple gravitational settlement were obtained by drawing samples from tappers' buckets, sieving, ammoniating, and allowing to stand for 48 hours. After sludge deposition had taken place, a sample of the supernatant latex was carefully withdrawn and its specific gravity was determined. The test sample was then returned to the bulk and, after thorough shaking, the specific gravity was again determined. In Table VI results are presented for seven random samples drawn on two occasions from different tappers' buckets.

It is seen from Table VI that the specific gravity differences obtained after settlement for 48 hours, while by no means uniform, can be appreciable and in some cases of the order of -0.004 .

TABLE VI
SPECIFIC GRAVITY VARIATIONS CAUSED IN NORMAL PRESERVED LATEX BY A GRAVITATIONAL SETTLEMENT OF 48 HOURS

Sample	Specific Gravity after Usual Shaking	Specific Gravity of Supernatant Latex after Deposition of Solids	Difference Due to Deposition of Solids
1	0.9761	0.9727	-0.0034
2	0.9802	0.9770	-0.0032
3	0.9740	0.9709	-0.0031
4	0.9681	0.9634	-0.0047
5	0.9670	0.9658	-0.0012
6	0.9712	0.9692	-0.0020
7	0.9685	0.9674	-0.0011

It was next sought to obtain some information on the closeness of approach of specific gravities of centrifugal concentrates to those presented for normal preserved latex in Table V. Sixty-eight samples of centrifugal concentrate, most of them supplied by courtesy of Dunlop Plantations Ltd., were examined for dry rubber content and specific gravity. The results were arranged in groups according to dry rubber content and the mean specific gravity and mean dry rubber content were calculated for each group. The values so obtained were then compared with the specific gravities indicated in Table V for normal preserved latex at the appropriate dry rubber contents. The data so obtained are presented in Table VII.

TABLE VII
INDIVIDUAL SAMPLES OF CENTRIFUGAL CONCENTRATE

Group D. R. C.	No. of Samples Examined	Mean D. R. C.	Mean S. G.	Deviation from Value for Normal Latex (See Table IX)
1	2	3	4	5
56.1-58.0	6	57.2	0.9476	-0.0039
58.1-59.0	10	58.6	0.9458	-0.0040
59.1-60.0	21	59.6	0.9442	-0.0045
60.1-61.0	31	60.4	0.9426	-0.0052

It is seen that in each group the specific gravity lies, as was expected, below the corresponding value for normal latex. The extent of the deviation approximates to -0.004 to -0.005 from the value derived from Table V for normal latex, and is seen to be in general greater but of the same order as that observed in Table VI when normal preserved latices are allowed to deposit solids by settling. If the specific gravity values for centrifugal concentrate are related, not to the values set out in Table V, but to those obtained by extrapolation of the figures of the Rubber Trade Association, which are themselves similar to those of de Vries,^{1,2} the deviations are much greater than those obtained when normal preserved latex is allowed to settle and are of the order of -0.01 . The inference is therefore again possible that, in the higher zones of dry rubber content, the values of de Vries and the Rubber Trade Association are high.

Further confirmation was next sought in a somewhat different manner. A single small bulk of latex was centrifuged and the skim latex and centrifugal concentrate from it were collected separately. By mixing the skim and cream fractions in varying proportions, clarified latices were obtained having dry rubber contents over a range from 16 to 57 per cent approximately, and specific gravity and dry rubber content values were obtained over this range. The results are set out in Table VIII.

TABLE VIII
SPECIFIC GRAVITY AND DRY RUBBER CONTENT OF MIXTURES OF CENTRIFUGAL CONCENTRATE AND SKIM LATEX FROM A SINGLE PARENT LATEX

D. R. C. <i>t</i>	S. G. <i>s</i>
56.7	0.9480
55.2	0.9497
54.0	0.9513
52.7	0.9523
51.0	0.9548
48.1	0.9582
45.0	0.9626
41.1	0.9668
37.4	0.9705
34.2	0.9743
30.5	0.9788
23.5	0.9870
19.6	0.9922
15.7	0.9970

By the same procedure as that outlined in the calculation of the equation of the most probable line for normal latex, the equation of the line best representing the values in Table VIII was calculated. The equation was found to be $s = -0.001187t + 1.0153$, and from it a dry rubber content—specific gravity relationship can be calculated and compared with that set out in Table V for normal latex. This comparison is made in Table IX.

Little or no importance can be attached to the fact that the deviations of the specific gravities of the artificial clarified latices, from those for normal preserved latices, are throughout the whole dry rubber content range of Table IX of the same order as the deviations shown by the 68 individual samples of centrifuged latex in Table VII; it must be remembered that the whole series of skim-cream mixtures represents only one single parent latex and that, by virtue of inherent differences in the specific gravity of the serum phase, different parent latices must yield slightly different lines for the skim-cream mixtures derived from them. The fact that, in this particular instance, the deviations at various dry rubber content

TABLE IX

SPECIFIC GRAVITY OF A SINGLE SERIES OF SKIM-CONCENTRATE MIXTURES COMPARED WITH SPECIFIC GRAVITIES FOR NORMAL PRESERVED LATEX

D. R. C.	Centrifugal Cream-Skim Mixtures	Specific Gravity of Normal Preserved Latex	Deviation from Specific Gravity of Normal Preserved Latex
35	0.9738	0.9772	-0.0034
40	0.9678	0.9714	-0.0036
50	0.9559	0.9598	-0.0039
55	0.9500	0.9540	-0.0040
56	0.9488	0.9529	-0.0041
57	0.9476	0.9517	-0.0041
57.2	0.9474	0.9515	-0.0041
58	0.9465	0.9505	-0.0040
58.6	0.9457	0.9498	-0.0041
59	0.9453	0.9494	-0.0041
59.6	0.9446	0.9487	-0.0041
60	0.9441	0.9482	-0.0041
60.4	0.9436	0.9478	-0.0042
61	0.9429	0.9471	-0.0042
62	0.9417	0.9459	-0.0042
65	0.9381	0.9424	-0.0043
80	0.9203	0.9251	-0.0048
100	0.8966	0.9019	-0.0053

values are all of the right order, amounts in all probability to little more than a coincidence. Some importance may, however, reasonably be attached to the single value for the specific gravity of the rubber phase at a dry rubber content of 100 per cent because, while skim-cream mixtures derived from different parent latices would be expected to give lines of slightly different slope, these lines would all be expected to give approximately the same value for specific gravity at dry rubber content of 100 per cent. This figure is, therefore, one upon which comparison may be made with that obtained for normal latex. The value actually derived is seen from Table IX to be 0.8966 which deviates by -0.0053 from the value of 0.9019 found in the present work for the rubber disperse phase in normal preserved latex. This deviation is again of the same order as those presented in Tables VI and VII but, if the value of de Vries and that derived from the Rubber Trade Association table for the specific gravity of the rubber disperse phase had been taken as the criterion from which to judge the deviation, it would then have been of the order of -0.017 which is much greater than would be expected from the experiments which are summarized in Table VI. These results lead also to the inference that a value of the order of 0.912-0.914 for the specific gravity of the rubber disperse phase in preserved latex is probably high.

Discussion and Summary

A specific gravity-dry rubber content table (Table V) has been obtained from the examination of a large number of samples of preserved latex. This table differs slightly from that adopted by the Rubber Trade Association, London.

A value of approximately 0.902 has been derived for the specific gravity of the rubber disperse phase in normal preserved latex, and this value is in good agreement with the value of 0.901 obtained by Scholtz and Klotz³ with fresh latex.

Experiments with individual samples of commercial centrifugal concentrate have indicated that, as a result of the removal of heavy solids, specific gravities of centrifugal concentrates may be expected to lie from 0.004 to 0.005 below the corresponding values for normal preserved latex.

Preliminary experiments with mixtures of the centrifugal concentrate and the skim latex obtained from a single parent latex have indicated that the value for the specific gravity of the true rubber phase in latex probably lies even below the value of 0.902 deduced from the examination of normal preserved latex.

The assistance given in this work by Inche Abdul Wahid bin Abdul Wahab and Mohamed Dom bin Sali is gratefully acknowledged.

References

- ¹ de Vries, *Archief Rubbercultuur*, **3**, 202 (1919)
- ² de Vries, *Ibid.*, **10**, 15 (1926).
- ³ Scholtz and Klotz, *Kautschuk*, **7**, 142 (1931).
- ⁴ Bishop and Fullerton, *Rubber Research Inst Planting Manual No. 4*, H-1 (1932).
- ⁵ Feldman, "Biomathematics," London, **1523** p. 345.

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Diffusion of Water through Organic Insulating Materials

D. B. Herrmann

CHEMICAL LABORATORIES, BELL TELEPHONE LABORATORIES, INC.

Water has remarkable penetrating power. No organic substance is known to be entirely impervious to it. The life of plants and animals may be said to depend on the diffusion of water through their cell walls, and it is a familiar fact that the water which permeates the human body forms its largest single component. Water passes through materials often considered water-proof such as rubber, asphalts, and waxes.

In the Bell System a number of organic materials are used as insulations which often are exposed to moisture. Though the actual quantity of water which diffuses

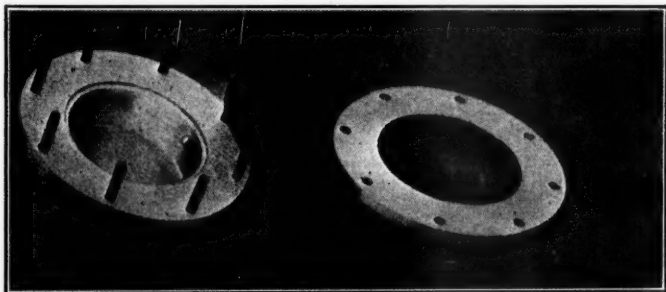


Figure 1—Water Vapor Passes from the Interior of the Aluminum Cell through the Rubber Sample into a Drying Agent Outside

through most organic substances is small, this small amount becomes important in condensers, coils, and terminal boxes and other apparatus which must be protected over a period of years.

One of the methods used to evaluate insulations which are to be exposed to moisture is the measurement of the quantity of water absorbed. Such measurements do not always give a complete picture of water-proofing characteristics, since a considerable amount of water may diffuse through a layer of material into some interior space and only a small amount remain absorbed in the outer layer. Differences in molecular structure, phase relationships, and crystalline state may play important roles in diffusion, and often the absorption of water does not appear to be the principal controlling factor.

Of the general methods for determining the rate of diffusion of water through a layer of substance, probably the most simple and direct is to establish on one side a concentration of water vapor, maintain on the other side a lower concentration, and measure the amount of water which passes through the material in a given time. A convenient way to do this is to seal a sheet of the material across a cup or cell in such a manner that moisture passes from the cell through the sample into a drying agent outside. For such measurements several types of cells are used in these Laboratories depending on the nature of the material.

* Reprinted from the October, 1934, issue of the Bell Laboratories Record.

For rigid and semi-rigid substances like soft and hard rubber, phenol fiber, cellulose derivatives, and many plastics, an aluminum cell is used in which the sample is held in place by an aluminum pressure ring, the seal being completed by suitable washers coated with petrolatum (Fig. 1). The cell is placed in a desiccator containing a drying agent and maintained at 25° C. by immersion in a water bath (Fig. 2). The loss in weight of the entire cell combination is taken as the amount of water which has diffused through. Moisture absorbed by the material does not change the total weight.

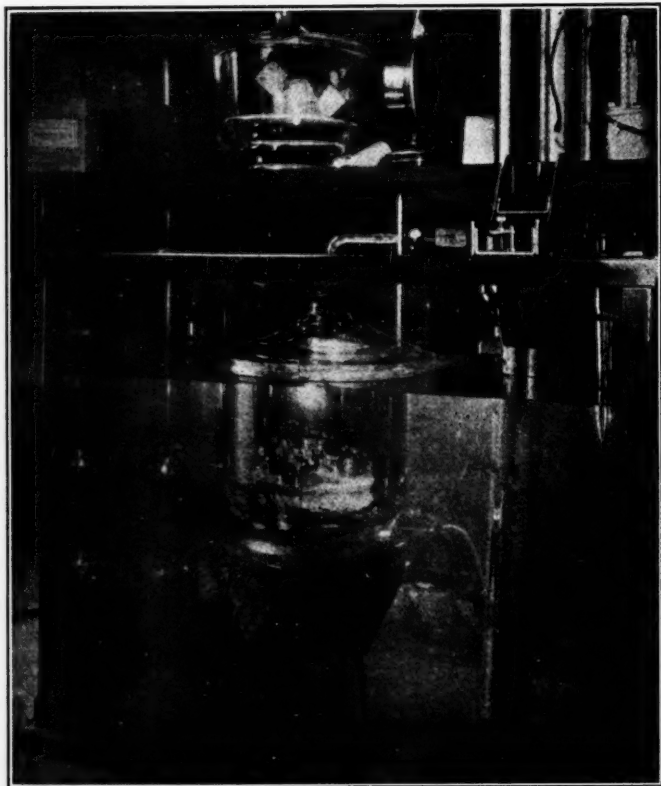


Figure 2—The Temperature Is Held Constant During a Diffusion Test Often by Keeping the Cells in a Desiccator Immersed in a Water Bath

For substances having a tendency to cold flow, such as asphalts, the cell shown in Fig. 3 is used. The asphalt is supported by a thin aluminum disc, and the drying agent is supported on a calibrated quartz spring whose elongation indicates the amount of water which has passed through.

A third type of cell is used for materials having a very low diffusivity and which require an extremely tight seal. Such a cell may be constructed by making a thick-walled wax cup, across the mouth of which a thin disc of the material to be measured may be sealed. The sealing is accomplished by melting together the edges of the cup and the disc, if the disc is of wax, or by melting the cup around

the edge of the disc if the latter cannot easily be melted. The water which passes through is collected by a drying agent attached to a calibrated quartz spring, as shown in Fig. 4. The temperature is kept constant by placing the apparatus in an air bath or constant temperature room.

Most materials obey quite closely the linear diffusion law established by Fick, and since the factors which enter into linear diffusion are definite and measurable,

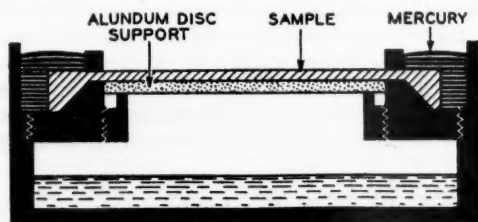


Figure 3—When a Material with a Tendency to Cold-Flow Is Placed in a Diffusion Cell, It Is Usually Supported by an Alundum Disc

the law is particularly applicable from an engineering standpoint. It states substantially that the amount of vapor diffusing through a unit area of a material in unit time is proportional to the difference in vapor pressures on the two sides and inversely proportional to the thickness. The constant of proportionality, or diffusivity constant, depends principally on the nature of the material. The law

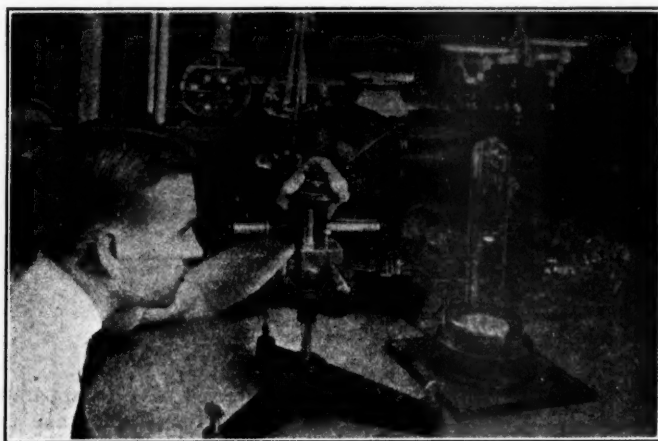


Figure 4—In Testing Substances Having a Tendency to Cold-Flow, Such as Asphalt, the Water Which Passes Through Is Collected by a Drying Agent Attached to a Calibrated Quartz Spring, as Shown Here

is somewhat analogous to Ohm's law; the differential vapor pressure corresponds to the electromotive force, and the flow of water molecules driven by it is checked by the "resistance" of the material. Diffusivity is thus analogous to conductance.

The diffusivity constant of a material is taken as the number of grams of water which pass through a one-centimeter cube in one hour under a vapor pressure difference of one millimeter of mercury at a definite temperature.

Organic materials whose diffusivity constants at 25° C. have been measured in the Laboratories include soft and hard rubber compounds, submarine cable insulations, phenol fiber and similar materials, cellulose acetate and related substances, asphalts, and pure hydrocarbons such as polystyrene. The amount of water which diffuses through a centimeter cube of material at 25° C. ranges between 10^{-9} and 10^{-5} grams per hour when the difference in vapor pressures is one millimeter of mercury (Fig. 5).

Measurements of this sort have proved especially valuable in dealing with rubber, asphalts, and waxes, which are used extensively in the Bell System as insulating materials, primarily to provide protection from water. The amount of material needed for protection has hitherto been determined largely empirically, but a knowledge of the rate at which water passes through an insulation now makes it

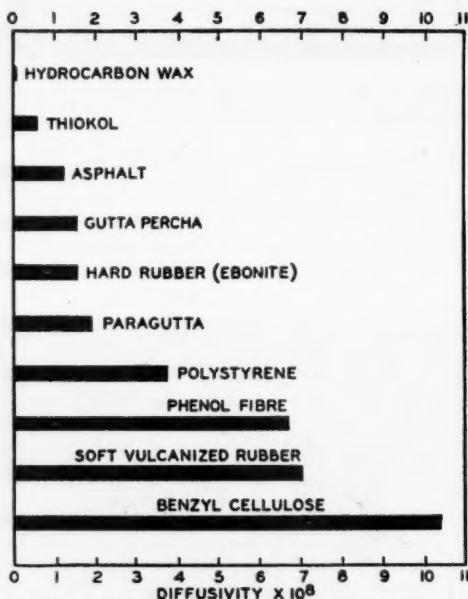


Figure 5—The Diffusivities of Organic Insulating Materials Differ Considerably. That of Cellulose Acetate, if Plotted on This Chart, Would Appear as a Bar Extending to 160.

possible to estimate the thickness needed to protect a piece of apparatus for a specified length of time under known conditions of temperature and humidity. The minimum thickness of rubber sheath necessary to protect a dry-core paper cable can be calculated, for example, and the amount of material required in sealing apparatus with an organic substance can be estimated.

The mechanism by which water diffuses through solid materials is not definitely known. There are some data on the diffusion of gases through inorganic substances, however, which help to explain similar processes in organic materials.

There are indications that sorption* plays an important part in some cases of the diffusion of gases through inorganic materials. Hydrogen diffuses into copper only after it has first been adsorbed on the copper surface, and palladium sorbs

* "Sorption," and the corresponding verb, "sorb," describe a process in which both absorption and adsorption takes place.

hydrogen so strongly as to indicate that they combine chemically. On the other hand, diffusion independent of adsorption seems to be exemplified by the passage of inert gases through fused silica, where the gas molecules are believed to enter extremely minute cracks in the film directly from the gas phase.

The diffusion of moisture through certain organic substances, such as polystyrene and hydrocarbon wax, is associated with very little absorption. The amount of water absorbed by polystyrene is extremely small, although the diffusion of water through it is comparatively large. The water absorption of the wax is also small, yet its diffusivity is only about one-fortieth of that of the polystyrene. Both materials are homogeneous, non-polar compounds. The difference between their diffusivities appears to be due to differences in their physical and chemical structure of some other sort than those determining sorption. In sharp contrast is the case of cellulose acetate, through which moisture passes 1600 times as fast as through hydrocarbon wax. Here the sorption of water is strong and probably borders on chemical union, as does the interaction of palladium with hydrogen. It is very likely that the higher sorption affects the diffusivity, and that both are largely accounted for by the same features of chemical structure.

To arrive at a true picture of the mechanics of moisture diffusion through organic substances much additional work is required. The measurements made in these Laboratories form only a beginning in this direction.

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A Water Bath Having Submerged Individual Sample-Containers for the Accelerated Aging of Rubber in Air

William L. Holt and Archibald T. McPherson

NATIONAL BUREAU OF STANDARDS, WASHINGTON, D. C.

Improved equipment for conducting the familiar Geer aging test on rubber has recently been installed at the National Bureau of Standards. This equipment consists of thermostatically controlled water baths in which small air ovens are

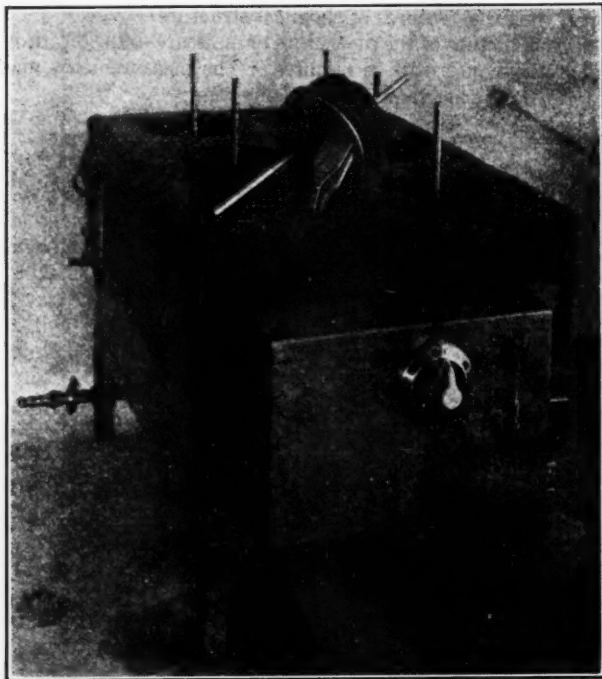


Figure 1—A Water Bath with Individual Containers with the Cover of One Container Removed to Show Method Employed in Holding Samples

submerged. Each oven serves for the accelerated aging of samples of a single composition, and thus avoids the possibility of contamination, which may be an important factor when samples of different compositions are aged in the same oven. The apparatus differs from that described recently by Milligan and Shaw¹ in that individual sample containers are employed and air circulation is obtained by convection.

A photograph of one water bath is shown in Fig. 1. In the illustration one container is shown open with test strips attached to the cover. The water bath is of a common size and type, with inside dimensions of $18 \times 12 \times 8\frac{3}{4}$ inches. The interior is lined with copper, and the exterior is of monel metal and encloses a layer of thermal insulation one inch in thickness on the bottom, sides, and top. This insulation is supplemented by a cover made from a woolen blanket which is fitted over the sides and the top.

The bath is heated by calrod units distributed in the water near the bottom. When these are operated at low heat, 440 watts, and controlled by a sensitive bimetallic thermoregulator, the temperature of all parts of the bath at levels

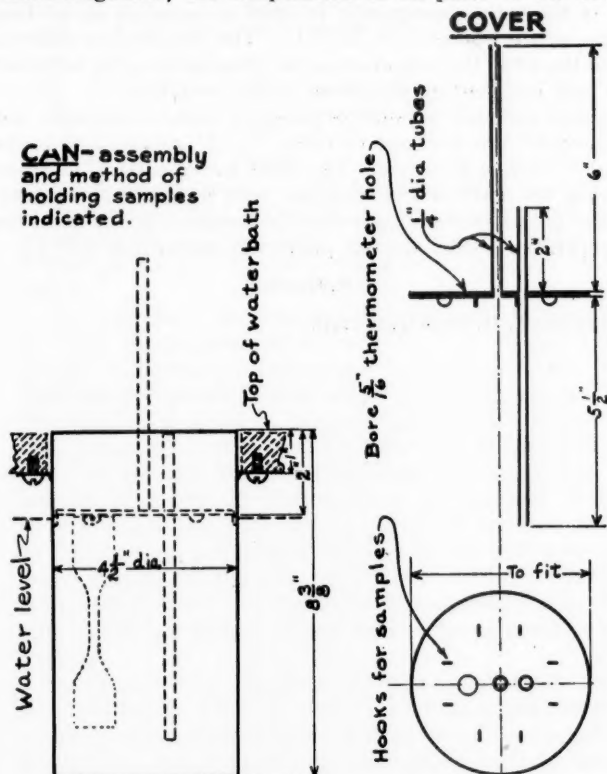


Figure 2—Construction of Individual Containers. The Material Used Is Nickel-Plated Brass. Method of Holding Samples Is Also Indicated

occupied by the sample containers is maintained within 0.2° or 0.3° C. without mechanical stirring. Under the usual operating conditions the heater is on about 25 per cent of the time.

The dimensions and construction of a sample-container are shown by the drawing in Fig. 2. The container consists of a nickel-plated brass cylinder $4\frac{1}{2}$ inches in diameter and $8\frac{3}{8}$ inches in height, with a cover which rests on a flange inside the cylinder about 2 inches from the top. The space above the cover is filled with thermal insulation made from discs of woolen blanket. Circulation of fresh air is secured by means of tubes, $\frac{1}{4}$ inch in inside diameter, mounted in the cover;

one of these extends to within about $\frac{1}{2}$ inch of the bottom of the container, and the other rises 6 inches above the cover. The exposed portion of the latter tube is insulated by a cylinder made from cork stoppers about 1 inch in diameter.

A rough measure of the rate of air circulation was obtained by placing naphthalene in the bottom of the container and observing the rate of evaporation. The naphthalene evaporated at a rate which indicated an air flow of 2 to 3 liters per hour. Since the volume of the container is about 1650 cc., this corresponds to an air change of about once or twice an hour. This rate of air circulation does not seriously affect the uniformity of temperature within the containers.

The temperature of the air in the containers was observed to be about 0.5°C . below that of the bath, consequently in order to maintain an air temperature of 70.0°C . the bath is operated at 70.5°C . The temperature difference between the bath and the air in the containers is due principally to the introduction of cold air, and to heat loss through the covers of the containers.

Thermometers mounted in different positions within a container indicated that the air temperature was constant to within 0.2°C . except close to the walls and within about $\frac{1}{2}$ inch of the cover. The cover was about 1.5°C . below bath temperature, while the walls of the container were at bath temperature. Thermocouples placed in test pieces hung within the container in the usual way indicated that the temperature within the test pieces was constant to 0.2°C .

Reference

- ¹ *J. Sci. Instruments*, **11**, 10-14 (Jan., 1934).

Manganese Salts in Plantation Rubber

G. A. Sackett

THE GOODYEAR TIRE & RUBBER COMPANY, AKRON, OHIO

ALTHOUGH it has been generally admitted for years that manganese salts have a deleterious effect on rubber, there are few data in the literature to show how the vulcanized product would be affected if it were made from a crude rubber containing an abnormally large amount of manganese. The receipt of a large shipment of plantation ribbed smoked sheets which analysis showed to contain an excessive amount of manganese led to this investigation.

The early literature contains little information regarding the effect of manganese on rubber. De Vries (6) stated that the use of potassium permanganate for washing or disinfecting sheets showed no harmful effects on the rubber, and that the addition of traces of permanganate to latex to prevent mold formation on the sheets made from the latex would not cause tackiness. Bruni and Pelizzola (3) found that the presence of abnormally high amounts of manganese resulted in tackiness of the crude rubber. They showed that 0.0001 to 0.0003 per cent of manganese might be expected in normal, sound rubber, and the presence of 0.001 to 0.005 per cent of manganese resulted in a moderate degree of tackiness, while 0.01 to 0.02 per cent of manganese resulted in a very tacky material.

Bishop and Sekar (2), carrying out investigations to ascertain the effect of certain proprietary solutions which consisted mainly of permanganates and which appeared on the market for the purpose of preventing mold formation on lightly smoked or unsmoked sheet, concluded: (1) The presence of manganese in amounts more than normal results in tacky rubber, and (2) the rate of cure of a rubber-sulfur stock is decreased by the addition of permanganate.

Akhurst (1) investigated the manganese in Malayan soils in order to ascertain whether rubber trees grown in a location abnormally rich in manganese would yield a product that was richer in manganese. In no case did he find manganese present in sufficient amounts to produce a deleterious effect on the rubber.

Taylor and Jones (5), investigating the effect on a tread stock of manganese and other metals that might be present

in softeners used in rubber compounding, found that 0.1 per cent of manganic oleate in a stock caused poor aging in the Bierer-Davis bomb and in the Geer oven tests. The manganese was added as a fatty acid salt directly before vulcanization. The results did not show the effect which a reaction between the crude rubber and manganese over a period of time before vulcanization would have had on the vulcanized product. The accelerator used was not stated, and the study was limited to a single tread stock, no comparison being made in a gum stock; nor was any study made of the effect of using an antioxidant.

Jones and Craig (4) investigated the effect of antioxidants on stocks containing copper and found phenyl- β -naphthylamine very effective in protecting the stock against the effects of this metal. The study was not extended to cover manganese.

During a storage period of about two years several bales of smoked sheets produced on a single European estate became very soft. An analysis of this rubber showed the presence of abnormal amounts of manganese. All the bales in this single lot were not tacky, but all showed approximately the same manganese content. When this lot was first received it was marked as first grade European plantation smoked sheets.

The sheets did not have the characteristic odor of smoke. Therefore it was first thought that they might have been made from latex which had been treated with a proprietary solution containing manganese. Investigation showed, however, that the sheets had been made in the regular way, and all conditions, except one, were normal to any of the plantations. The single abnormality was the water supply for dilution of latex and spraying the rollers of the sheeting machines. Analysis showed this water to contain 22 parts of manganese per 100,000.

EXPERIMENTAL PROCEDURE

Although both Bruni and Pelizzola (3) and Bishop and Sekar (2) suggested methods of determining manganese in rubber, the following procedure was developed, since it was found to be faster and quite accurate:

A 20-gram sample of rubber is ashed in a large porcelain crucible, starting over a gas flame and finishing in an electric muffle furnace. After cooling, the ash is taken up with 25 ml. of a 35 per cent solution of nitric acid and digested on the hot plate for about half an hour. It is then diluted with 25 ml. of distilled water and transferred, filtering if necessary, to an Erlenmeyer flask. Ten milliliters of a 10 per cent silver nitrate solution are added to catalyze the oxidation reaction, and the mixture is brought to a boil; then 10 ml. of a 10 per cent solution of ammonium persulfate are added, and the resultant mixture is allowed to stand for 5 or 10 minutes in order to develop fully the permanganate color. The mixture is cooled and diluted to

approximately 100 ml. and titrated to the disappearance of the permanganate color in the usual manner, using a standard solution of sodium arsenite. A convenient concentration is 0.005 *N* equivalent to 0.055 mg. of manganese per ml. of solution. The reagents should be manganese-free.

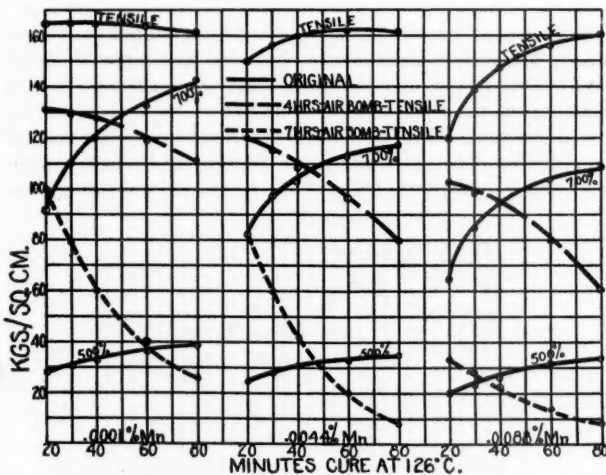


FIGURE 1. EFFECT OF LOW PERCENTAGES OF MANGANESE ON PROPERTIES OF FORMULA 1

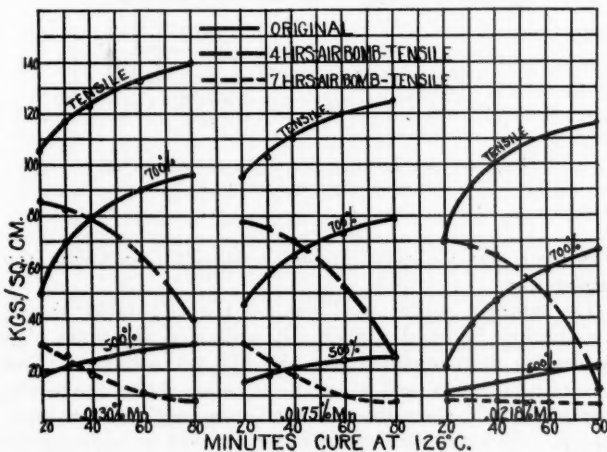


FIGURE 2. EFFECT OF HIGH PERCENTAGES OF MANGANESE ON PROPERTIES OF FORMULA 1

Samples of smoked sheets from several known estates, together with a sample of the soft rubber previously mentioned, were analyzed by the method described, and the following results obtained:

ESTATE	CONDITION OF RUBBER	% Mn
A	Soft, tacky ^a	0.0218
B	Normal	0.0001
C	Slightly soft	0.0007
D	Normal	0.0003
E	Normal	0.0001

^a Part of this rubber was normal but showed the same percentage of manganese.

In order to discover the effect of varying amounts of manganese, the rubber from estates A and B was blended in different proportions, and the percentage of manganese in each mixture was then calculated. The rubber from these estates was also analyzed for copper and iron, and in no case was the amount found to be in excess of a trace, which is a normal condition. A determination of the fatty acid present showed

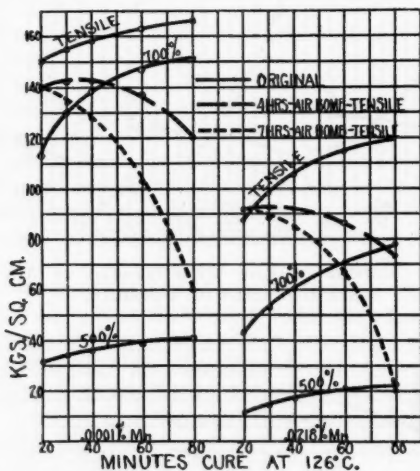


FIGURE 3. EFFECT OF MANGANESE ON PROPERTIES OF FORMULA 2

that there was sufficient present naturally to activate the accelerators.

The estate A rubber used was not the soft, tacky sheets, but the firm, normal rubber. It contained the same high percentage of manganese but had not yet softened. This type of rubber was used, since it was believed that the results obtained would show the effects of using such rubber innocently. Tacky rubber would never be used in high-quality compounds, but normal-appearing rubber would. The tests were carried out in gum stocks using mercaptobenzothiazole, diphenylguanidine, and a plain rubber-sulfur mixture, and in a tread stock using mercaptobenzothiazole. The effect of adding phenyl- β -naphthylamine was observed in the mercaptobenzothiazole stocks. Age resistances were determined only in accelerated tests which varied with the stock

under consideration. Flex life and abrasion resistance were determined in the tread stock.

The following mixtures were made for the study of the gum stocks:

ESTATE A	ESTATE B	CALC. Mn
%	%	%
0	100	0.0001
20	80	0.0044
40	60	0.0088
60	40	0.0130
80	20	0.0175
100	0	0.0218

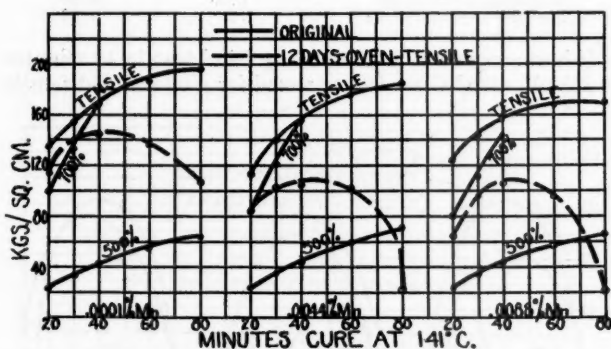


FIGURE 4. EFFECT OF LOW PERCENTAGES OF MANGANESE ON PROPERTIES OF FORMULA 3

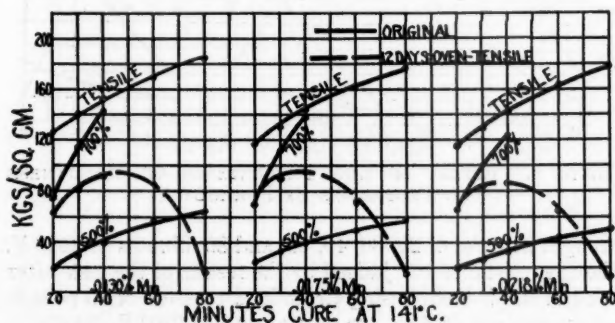


FIGURE 5. EFFECT OF HIGH PERCENTAGES OF MANGANESE ON PROPERTIES OF FORMULA 3

The following blended proportions were used in the tread stocks:

ESTATE A	ESTATE B	CALC. Mn
%	%	%
0	100	0.0001
25	75	0.0055
50	50	0.0110
75	25	0.0164
100	0	0.0218

The formulas used for testing the rubber are given in the following paragraphs. The accelerators and antioxidants were the regular commercial grades and were not specially tested or purified for this work.

MERCAPTOBENZOTHAZOLE GUM STOCKS

The formulas of the mercaptobenzothiazole gum stock used are as follows:

Formula No.	1	2
Rubber	100.00	100.00
Zinc oxide	4.00	4.00
Sulfur	6.00	6.00
Mercaptobenzothiazole	0.50	0.50
Phenyl- β -naphthylamine	...	1.00

This stock gave a "best cure" by hand tear in 40 minutes at 258° F. (126° C.). It was tested for modulus and tensile

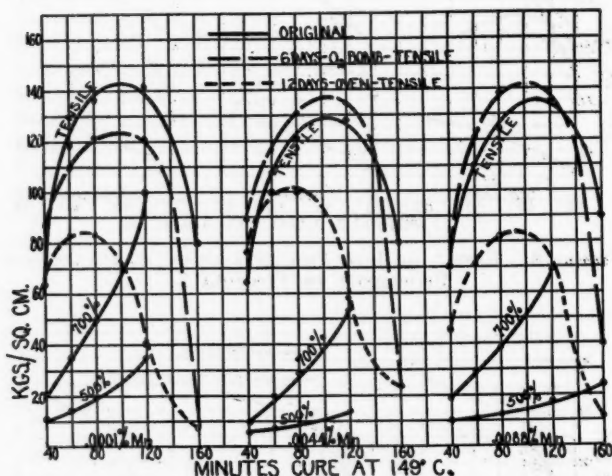


FIGURE 6. EFFECT OF LOW PERCENTAGES OF MANGANESE ON PROPERTIES OF FORMULA 4

strength at cures of 20, 30, 40, 60, and 80 minutes at 258° F. The age resistance was judged by the results of the tests after aging in an air bomb, using air under a pressure of 80 pounds per square inch (5.6 kg. per sq. cm.) and at 236° F. (113° C.). The stock was aged for periods of 4 and 7 hours.

The results obtained are plotted on Figures 1, 2, and 3. The effect of using an antioxidant was tested only with the original samples, since it was believed that the whole series of blends was unnecessary to show the results.

A study of the data obtained shows that in these stocks manganese produces lower tensile strength and modulus in both original and aged samples. Judging from hand tear, the rate of cure is not greatly affected by the presence of manganese. The use of an antioxidant greatly improves the age

resistance of the stocks but does not greatly affect the original tensile and modulus values.

The effect of increasing manganese content on the age resistance of these stocks is probably more easily seen by com-

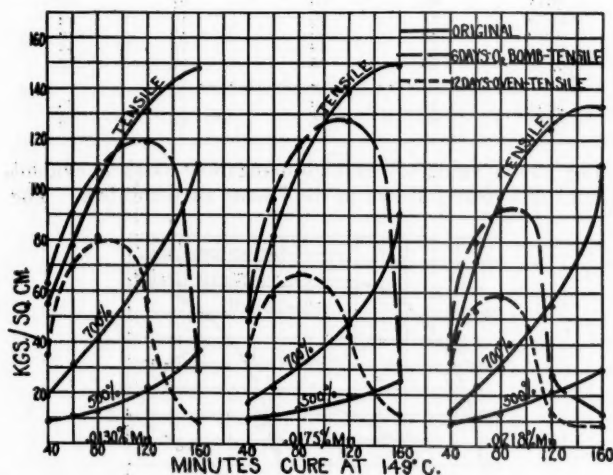


FIGURE 7. EFFECT OF HIGH PERCENTAGES OF MANGANESE ON PROPERTIES OF FORMULA 4

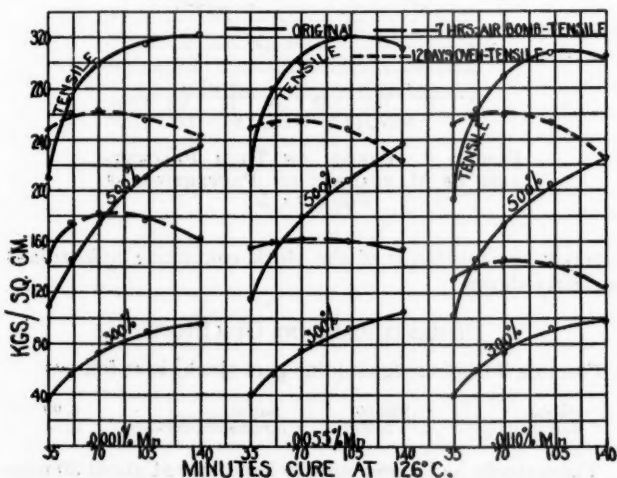


FIGURE 8. EFFECT OF LOW PERCENTAGES OF MANGANESE ON PROPERTIES OF FORMULA 5

paring the tensile ratios of the best cure and the average tensile ratio of all cures as follows (tensile ratio is the ratio of the tensile strength of the aged sample to that of the original):

MANGANESE %	AGED 4 HOURS IN AIR BOMB		AGED 7 HOURS IN AIR BOMB	
	Total av. tensile ratio	Best-cure tensile ratio	Total av. tensile ratio	Best-cure tensile ratio
	%	%	%	%
FORMULA 1, NO ANTIOXIDANT				
0.0001	75	77	37	38
0.0044	66	70	27	27
0.0088	62	63	16	16
0.0130	59	65	16	15
0.0175	57	62	16	15
0.0218	55	65	7	7
FORMULA 2, WITH ANTIOXIDANT				
0.0001	84	89	71	80
0.0218	83	86	68	76

The poorer aging of the high-manganese stock is evident and is quite clearly shown in the 7-hour air bomb test. The

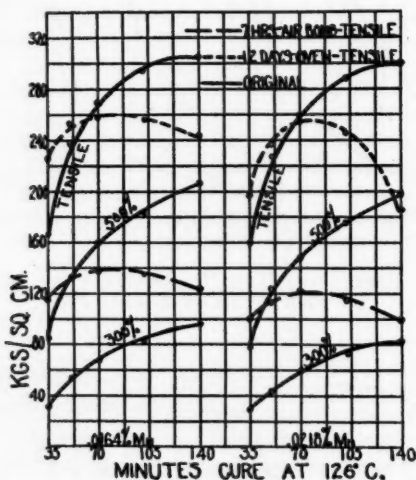


FIGURE 9. EFFECT OF HIGH PERCENTAGES OF MANGANESE ON PROPERTIES OF FORMULA 5

superior age resistance of the stock containing antioxidant is clearly shown.

DIPHENYLGUANIDINE GUM STOCK

Formula 3 (diphenylguanidine gum stock) is as follows:

Rubber	100.00	Sulfur	4.00
Zinc oxide	5.00	Diphenylguanidine	0.75

These stocks had a best cure by hand tear at about 30 minutes at 285° F. (141° C.). The cures tested were 20, 30, 40, 60, and 80 minutes at 285° F. The age resistance was judged from tests after exposure in a regular Geer oven for 12 days at 158° F. (70° C.). The results are plotted on Figures 4 and 5.

The best-cure tensile ratios and the average total tensile ratios for formula 3, oven-aged for 12 days, are as follows:

MANGANESE %	TOTAL AV. TENSILE RATIO	BEST-CURE TENSILE RATIO	MANGANESE %	TOTAL AV. TENSILE RATIO	BEST-CURE TENSILE RATIO
	%	%		%	%
0.0001	77	90	0.0130	45	57
0.0044	56	70	0.0175	49	69
0.0088	42	54	0.0218	48	68

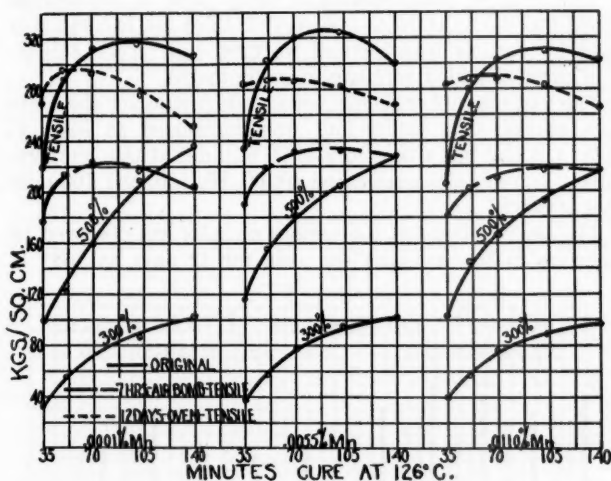


FIGURE 10. EFFECT OF LOW PERCENTAGES OF MANGANESE ON PROPERTIES OF FORMULA 6

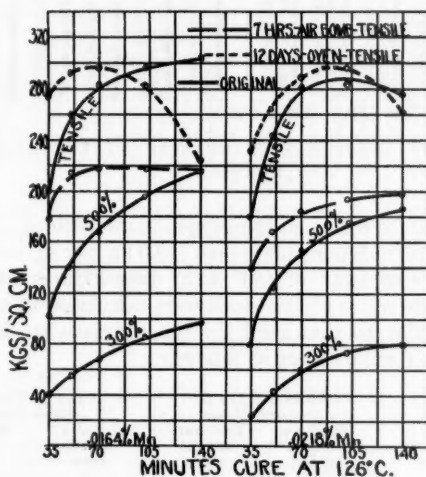


FIGURE 11. EFFECT OF HIGH PERCENTAGES OF MANGANESE ON PROPERTIES OF FORMULA 6

The effect of increased manganese content of the rubber is definitely seen. The original tensile strength and modulus values are not appreciably affected by the manganese, the differences appearing only on aging.

RUBBER-SULFUR STOCK

Formula 4 is as follows:

Rubber 100.00 Sulfur 10.00

This type of compounding is rarely used in commercial stock, but the formula, or one very similar to it, is commonly used by various investigators working with crude rubber. The effect of added accelerator is eliminated.

The various rubber blends were made just as for the other gum stocks. The compound was vulcanized at 300° F. (149° C.) and has a best cure of 60 minutes at this temperature. The samples were cured 40, 60, 80, 120, and 160 minutes at 300° F.

The age resistance of the various samples was observed by exposure in the regular Geer oven for 12 days at 158° F.

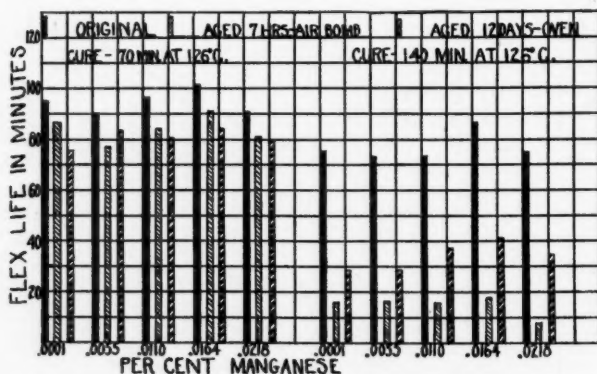


FIGURE 12. EFFECT OF MANGANESE ON FLEX LIFE OF FORMULA 5

(70° C.) and for 6 days in the oxygen bomb with oxygen pressure of 150 pounds per square inch (10.5 kg. per sq. cm.) and a temperature of 122° F. (50° C.). (See Figures 6 and 7.)

The tensile ratios of this stock were calculated in a manner exactly similar to that used for the previous stocks. The results with formula 4 are as follows:

MANGANESE %	AGED 6 DAYS IN OXYGEN BOMB		AGED 12 DAYS IN GEER OVEN	
	Total av. tensile ratio	Best-cure tensile ratio	Total av. tensile ratio	Best-cure tensile ratio
0.0001	85	96	58	71
0.0044	94	109	68	93
0.0088	95	116	52	69
0.0130	90	115	56	88
0.0175	86	110	49	72
0.0218	72	117	47	73

This stock is not satisfactory for showing the effect of increased manganese content. The tensile strength and modu-

lus values of the stock before aging are not greatly affected by the amount of manganese present. In this respect this stock differs from those tested previously. The tensile ratios of the stock aged in the oxygen bomb do not show a marked difference for the total average, while the best-cure ratios are all in excess of 100 per cent. This is due to the stiffening of the stock caused by the increase in cure at the rather low temperature of operation of the bomb. The results obtained after aging in the oven are more significant and indicate that an increase in the manganese content produces an inferior stock, which agrees with the author's previous findings.

TREAD STOCK

The heavy loading of tread stock with carbon black sometimes masks the effects of other variables. It is pertinent,

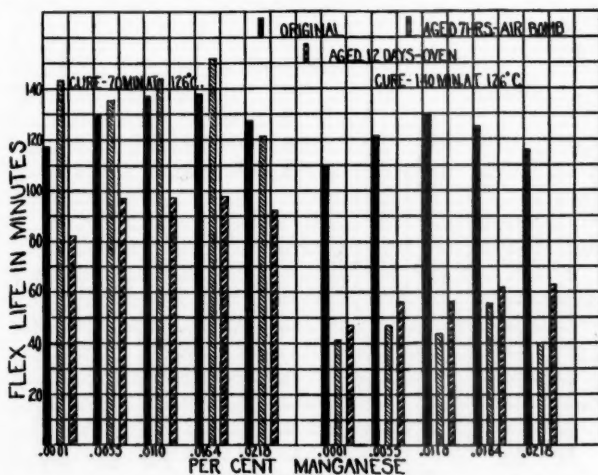


FIGURE 13. EFFECT OF MANGANESE ON FLEX LIFE OF FORMULA 6

therefore, to check the effect of increased manganese content in such a stock.

The stocks used for this study were as follows:

Formula No.	5	6
Rubber	100.00	100.00
Zinc oxide	6.00	6.00
Sulfur	3.00	3.00
Carbon black	40.00	40.00
Stearic acid	3.25	3.25
Pine tar	4.00	4.00
Mercaptobenzothiazole	1.25	1.25
Phenyl-β-naphthylamine	...	1.00

These stocks have a best cure by hand tear test in 70 minutes at 258° F. (126° C.). They were cured over a range of 35, 50, 70, 100, and 140 minutes at this temperature. The age resistance was observed both in the air bomb and in the Geer oven. The air bomb exposure was for 7 hours with an air

pressure of 80 pounds per square inch (5.6 kg. per sq. cm.) and a temperature of 236° F. (113° C.). The Geer oven had circulating air at 158° F. (70° C.).

In addition to the effect of these age tests on the tensile strength of the stock, their effect on flex life was tested with a De Mattia reciprocating flexometer and on abrasion loss with a du Pont abrasion tester. The cures used for the flex test were the best cure of 70 minutes and overcure of 140 minutes. The abrasion tests were made at a slight overcure—75 minutes at 258° F.

The tensile results for the stock without antioxidant are shown graphically in Figures 8 and 9 and with antioxidant on Figures 10 and 11. The flex test results are shown on Figures 12 and 13. The abrasion resistance tests are given on Figure 14.

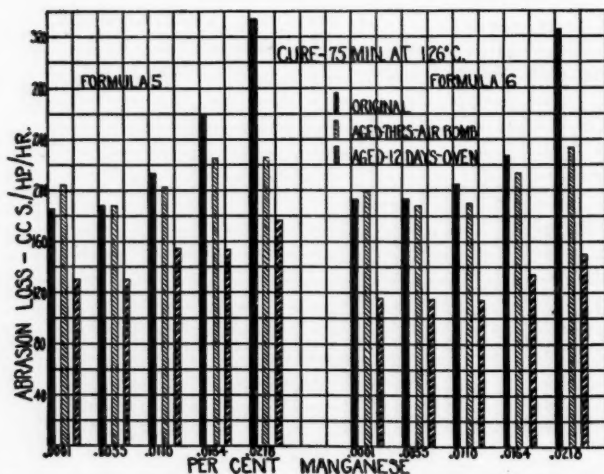


FIGURE 14. EFFECT OF MANGANESE ON ABRASION LOSS OF FORMULAS 5 AND 6

In a manner similar to that used for the gum stocks, the following tensile ratios were calculated for the tread stocks:

MANGANESE %	AGED 7 HOURS IN AIR BOMB		AGED 12 DAYS IN GEER OVEN	
	Total av. tensile ratio %	Best-cure tensile ratio %	Total av. tensile ratio %	Best-cure tensile ratio %
FORMULA 5, NO ANTIOXIDANT				
0.0001	60	60	93	90
0.0055	57	54	88	83
0.0109	50	51	84	90
0.0164	51	51	98	96
0.0218	45	45	94	100
FORMULA 6, WITH ANTIOXIDANT				
0.0001	72	71	96	93
0.0055	74	71	95	90
0.0109	74	77	102	95
0.0164	77	77	101	105
0.0218	71	67	106	103

This table shows that air bomb aging brings out the effect of increased manganese content to a more marked degree than does Geer oven aging. The use of an antioxidant reduces the deleteriousness of the manganese. The stock becomes stiffer in the oven during the 12-day period, so that this tensile ratio is of no value as a comparison index.

The effect of manganese in reducing the tensile strength and modulus values are evident from the figures. The air bomb aging shows much more change than does oven aging. The use of an antioxidant increases the age resistance of all samples about equally. The flex life is affected little by manganese, but the abrasion loss as measured on the machine used is influenced considerably; the use of phenyl- β -naphthylamine improves the flex life but not the abrasion resistance.

CONCLUSIONS

1. Abnormal amounts of manganese in crude rubber compounded in a gum type stock using mercaptobenzothiazole or diphenylguanidine result in lowered modulus and poorer age resistance.

2. The effects of abnormal amounts of manganese are not as evident in a rubber-sulfur stock as in stocks using an organic accelerator.

3. High-manganese rubber in a mercaptobenzothiazole tread stock gives lower modulus and the age resistance is poorer, but the effect is not as marked as in a gum stock.

4. Phenyl- β -naphthylamine in a gum or tread stock greatly improves the age resistance of a high-manganese rubber stock.

5. Rubber containing abnormally high percentages of manganese cannot always be detected by appearance; in order to avoid the bad effects of manganese in the vulcanized stocks, analysis of the crude rubber is necessary.

6. Because there is apparently no benefit to the crude rubber manufacturer through the use of manganese in any form, and because of the very bad effects on vulcanized stocks, every care should be exercised by the rubber producer to see that manganese salts are not introduced at any step in the process.

7. Rubber containing abnormally high percentages of manganese should not be used in high-quality stocks; when used, they should be blended with large proportions of normal rubber and used in a highly loaded stock containing an antioxidant.

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